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| <b>(54) Title:</b> ELASTOMERIC MASK AND USE IN FABRICATION OF DEVICES, INCLUDING PIXELATED ELECTROLUMINESCENT DISPLAYS   |           |   |
| <b>(57) Abstract</b><br><p>An elastomeric mask is provided that allows deposition of a variety of materials through mask openings. The mask seals effectively against substrate surfaces, allowing simple deposition from fluid phase, gas phase, and the like or removal of material using gaseous or liquid etchants. The mask then can be simply peeled from the surface of the substrate leaving the patterned material behind. Multi-layered mask techniques are described in which openings in an upper mask allow selected openings of a lower mask to remain unshielded, while other openings of the lower mask are shielded. A first deposition step, followed by re-orientation of the upper mask to expose a different set of lower mask openings, allows selective deposition of different materials in different openings of the lower mask. Pixelated organic electroluminescent devices are provided via the described technique.</p> <div data-bbox="868 1155 1421 1879" style="text-align: center;"> </div> |           |   |



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## ELASTOMERIC MASK AND USE IN FABRICATION OF DEVICES, INCLUDING PIXELATED ELECTROLUMINESCENT DISPLAYS

### Field of the Invention

5           The present invention relates generally to surface modification, and more particularly to the deposition of material onto a surface through openings in an elastomeric mask.

### Background of the Invention

10           In fields involving microelectronic devices, sensors, and optical elements, the development of devices that are small relative to the state of the art, controllable, and conveniently and relatively inexpensively reproduced with a relatively low failure rate is important.

          There is currently great interest in the fabrication of optical devices based on organic materials that display electroluminescence (Burrows, et al., *Current Opinion in Solid State and Materials Science*, 1997, 2, 236; Baigent, et al., *Synth. Meth.*, 1994, 67, 3). These devices  
15           could find application in a variety of settings, including flat panel optical displays. Electroluminescence, including in some cases organic electroluminescent materials, is described by Yam, "Plastics Get Wired", *Scientific American*, July, 1995, 83-87; Kijima, et al., "RGB Luminescence from Passive-Matrix Organic LED's", *IEEE Transactions on*  
20           *Electron Devices*, 44, 8, August, 1997; Shen, et al., "Three-Color, Tunable Organic Light-Emitting Devices", *Science*, 276, June 27, 1997; and Burrows, et al., "Achieving Full-Color Organic Light-Emitting Devices for Lightweight, Flat-Panel Displays", *IEEE Transactions on Electron Devices*, 44, 8, August, 1997. A variety of materials, including electroluminescent materials, have been deposited on surfaces at small feature size using a variety of techniques  
25           including laser ablation, photolithography, the use of shadow masks, and other techniques.

          Burger, et al., in "High-Resolution Shadow Mask Patterning in Deep Holes and its Application to an Electrical Wafer Feed-Through", *Sensors and Actuators*, A 54 (1996) 669-673, describe electron-beam evaporation of metals through a shadow mask.

          Wang, et al. in "identification of a blue photoluminescent composite material from a  
30           combinatorial library" *Science*, 279, March 13, 1998, 1712-1714, describe a quaternary combinatorial masking strategy used in conjunction with photolithography to generate compositionally diverse thin-film phosphor libraries.

Noach, et al., in "Microfabrication of an Electroluminescent Polymer Light Emitting Diode Pixel Array", *Appl. Phys. Lett.*, 69 (24), December 9, 1996, describe a technique for the fabrication of a light emitting diode array based on conjugated electroluminescent polymers sandwiched between appropriate electrodes. The method is based upon direct photoablation  
5 with an excimer laser.

Renak, et al., in "Microlithographic Process for Patterning Conjugated Emissive Polymers", *Adv. Mater.*, 1997, 9, 5, 392-394, describe a microlithographic process for patterning electroluminescent poly(p-phenylenevinylene) (PPV), and show preliminary results from pixel-like LED arrays prepared by this technique. Photoacid generators,  
10 molecules that generate acids upon photolysis, were used. A photoacid generator admixed with a PPV precursor is spin-cast onto a substrate, according to the technique, followed by

Development in chloroform washes away un-reacted precursor, leaving patterned PPV.

Granstrom, et al., in "Micrometer- and Nanometer-Sized Polymeric Light-Emitting  
15 Diodes", *Science*, 267, March 10, 1995, describe a technique for the fabrication of light-emitting diodes by polymerizing doped and conducting polymers electrochemically in randomly-distributed pores of commercially-available microfiltration membranes. Polycarbonate membranes were used. Electroluminescent polymer was spin-coated from xylene solution on top of a microfiltration membrane-contact structure.

20 While the above-described and other techniques may be advantageous in many circumstances, many require relatively sophisticated and expensive apparatus and/or require excessive numbers of steps or potentially destructive chemical techniques. For example, laser ablation is relatively slow and requires relatively complex apparatus. Also, it is limited in that pixels are defined by patterning cathode material rather than the electroluminescent material  
25 itself, and therefore the technique is not well-suited to creation of a multi-colored display. Photolithography is generally faster than laser ablation and therefore has greater potential for high-volume production of useful devices. However, wet chemical etching generally is required to define pixels using photolithography, which has a deleterious effect on electroluminescent efficiency. Lidzey, et al. (*Synth. Meth.*, 1996, 82, 141) report that the  
30 efficiency of an electroluminescent device was decreased by 60 percent upon one photolithographic step involving a wet chemical etch. Devices also can be degraded by exposure to atmospheric water and oxygen, inevitable during photolithography.

Encapsulation has been used as a technique to avoid degradation during photolithography (Tian, et al., *Appl. Phys. Lett.*, 1997, 71, 3197). Encapsulation, however, is problematic, according to Tian, et al., who report that it can lead to shorting of devices. Encapsulation also adds an extra step to the fabrication process. Shadow masking techniques that are known typically involve the use of machined-metal masks, in which the size of pixels are generally considered too large for high-resolution displays. In many of the above techniques, it is not possible to fabricate displays on non-planar surfaces.

Hebner, et al. in "Ink-Jet Printing of Doped Polymers for Organic Light Emitting Devices", *Appl. Phys. Lett.* 72, 5, Feb. 2, 1998, describe patterning luminescent-doped polymer films using ink-jet printing.

International patent publication WO 97/33737 (International patent application serial number PCT/US97/04005) of Kim, et al., entitled "Method of Forming Articles and Patterning Surfaces Via Capillary Micromolding", describes techniques for applying a variety of species to surfaces according to predetermined patterns. An elastomeric article having a contoured surface including a plurality of protrusions and intervening indentations is positioned against a substrate surface so that the outward-facing surfaces of the protrusions contact the substrate surface. In this way a plurality of channels are created, each defined by the surface of an indentation and a portion of the substrate surface in register with the indentation. A fluid carrier or precursor is introduced into the channels, an agent is deposited at regions of the substrate surface corresponding to the channels, and the article is removed from the surface. Patterned chemical reactions, precipitation, polymerization, and the like can take place at the substrate surface in this manner. Alternatively, an agent can be positioned in the indentations and the contoured surface brought into contact with a surface to be modified. Also described in Kim, et. al. is a flexible polymeric mask used to pattern deposition of material on a surface.

Rogers, et al., (*Appl. Phys. Lett.* 7, 70, 1997) describe a technique for forming a photomask on the exterior surface of an optical fiber. An elastomeric article, having a contoured surface including protrusions and intervening indentations, is used to apply a chemical species to the exterior surface of an optical fiber according to the pattern of the protrusions. Specifically, the axis of the optical fiber is positioned perpendicularly to the protrusions and is rolled across the protrusions, and rings of the chemical species are transferred from the protrusions to the outer surface of the fiber in this way. The chemical

species can facilitate creation of a photomask by serving as a metal deposition catalyst.

Several physical masking techniques are known for application of specific materials to specific portions of a surface.

Flexible masks are known for use in selective exposure of photoresist in a pattern  
5 corresponding to the pattern of the mask. U.S. Patent No. 4,735,890 (Nakane) describes a photomask for photolithographic fine patterning of a photoresist film. A thin film of a polymeric material having elasticity is brought into intimate contact with a photoresist film. Selective exposure of the photoresist through the photomask allows desired patterning of photoresist. Other "contact photolithography" techniques, involving contact between a mask  
10 and a photoresist coated substrate, are described in U.S. Patent Nos. 5,147,763 (Kamitakahara) and 5,160,959 (Everett) and 4,810,621 (Akkapeddi).

A thin film is provided on a substrate and a mask, having a desired pattern, is formed on the thin film by forming a layer of an organic resin on the thin film and forming the organic resin  
15 layer in a desired pattern by a mechanical forming member. An exposed portion of the thin film then is removed by etching.

U.S. Patent No. 4,518,636 (Richards) describes a technique for selective metal plating of a component. Upper and lower faces of the component are contacted with upper and lower masks, respectively, so that the lower mask exposes a part of the component to be plated. The  
20 part is positioned over a plating tank and selective plating takes place. The upper mask can be a deformable elastic polymeric material, and the lower mask is a more rigid rubber or plastic material.

U.S. Patent No. 5,480,530 (Zejda) describes an elastomeric mask for covering the outer marginal area of a disk-shaped substrate surface during a coating process. The substrate  
25 can be a compact disk, and the mask is of an annular shape with a circular opening into which the disk is placed. An inner, substrate holder, inserted into a central hole of the disk, also made of elastomeric material.

U.S. Patent No. 5,691,018 (Kelly) describes a flexible elastomeric mask for protecting apparatus used to mount a work piece to be subjected to thermal spray coating.

30 U.S. Patent No. 5,705,043 (Zwerner) describes apparatus for selectively electrolytically plating defined regions of a continuously moving conductive work piece. Elastomeric sealing plates are provided including openings that define areas of work pieces to

be plated.

Described above are several techniques for creation of a variety of materials, including electroluminescent materials, that in many cases are complicated and expensive. Also described above are several masking techniques, many of which do not recognize application to very small-feature, very high-resolution techniques. Accordingly, one object of the present invention is to provide high-resolution optical devices that can be multi-color and can display electroluminescence. Another object of the invention is to provide apparatus and techniques for forming such displays. It is another object of the invention to provide improved apparatus and techniques for forming a variety of patterns of a variety of materials on a variety of surfaces at high resolution.

#### Summary of the Invention

The present invention provides a series of methods for patterning a surface, and articles including patterns at surfaces.

In one aspect the invention provides a series of methods. One method involves shielding a first portion of a surface of an article with a masking systems including a cohesive mask in conformal contact with a surface of the article. An agent then is allowed to be applied through a channel in the masking system to a second portion of the surface of the article while the agent is prevented from being applied to the first portion. The channel has a dimension of less than one millimeter.

In another embodiment a method is provided that involves shielding a first portion of a surface of an article with a mask while leaving a second portion of the surface of the article remaining unshielded by the mask. The first portion has a dimension of less than one millimeter, and is shielded by positioning the mask in conformal contact with the surface without degrading a portion of the mask proximate the second portion of the surface. An agent then is applied to the second portion of the surface of the article.

In another method a first portion of a non-planar surface of the article is shielded with a mask by bringing a surface of the mask into conformal contact with the non-planar surface of the article an agent then is allowed to pass through a channel within the mask and to be applied to a second portion of the surface of the article while the agent is prevented from being applied to the first portion with the mask. The channel has a dimension of less than one millimeter. Another method involves shielding a first portion of a surface of an article with a

masking system by bringing a surface of the masking system into conformal contact with a surface of the article. An agent is allowed to be applied to a second, unshielded portion of the surface of the article while the agent is prevented from application from the first portion of the surface of the article with the masking system. The masking system then is re-placed, and an agent is applied to at least a portion of the first portion of the surface of the article.

In another method, a first portion of a surface of an article is shielded with a mask. A fluid is allowed to be applied to a second portion of the surface while the fluid is prevented from being applied to the first portion with the mask. The second portion of the surface has a dimension of less than one millimeter. A material is allowed to harden from the fluid, and the mask is removed from the surface while leaving the article adhere to the second portion of the surface.

by bringing a surface of the mask into conformal contact with the surface of the article while leaving a second portion of the surface of the article unshielded by the mask. The first portion that is shielded has a dimension of less than one millimeter. An agent then is applied to the second portion of the surface and, without exposure of the mask to conditions of degradation, the mask is removed from the surface thereby leaving the agent at the second portion of the surface and the first portion free of the agent.

The invention also provides a method according to any of those described above involving application of an agent to a specific portion of a surface of an article using a mask, followed by application of the same or another agent, via a second masking step involving the same or a different mask, to a portion of the surface such that the agent applied via the second step contacts at least a portion of the agent applied via the first masking step. The method can result in an interconnected pattern of agent on a surface, where the surface also includes regions free of the agent, which can define electrical circuitry or the like. This technique can be used with multiple re-placement steps to produce not only contacting, but intersecting agent deposition portions. For example, a pattern can be used to conduct multiple depositions, or applications, resulting in intersecting wires, or the like.

Another method of the invention involves immobilizing on average less than about  $1 \times 10^5$  at each of a plurality of separate, isolated regions of a surface of an article while leaving regions of the surface of the article intervening the separate isolated regions essentially free of the molecules.



In another aspect the invention provides an article that can be used for methods described herein or for other purposes. In one embodiment the article is an elastomeric article including a first surface and an opposing second surface, and plurality of channels passing through the article and connecting the first surface with the second surface. At least one of the plurality of channels has a cross-sectional dimension of less than one millimeter.

Another aspect of the invention involves making a mask. Generally, the method involves providing a master and forming the mask on a surface of the master, preferably by allowing a fluid precursor of the mask to at least partially solidify against the master. The fluid precursor can be a fluid polymer or prepolymer, which can be allowed to polymerize, crosslink, or solidify against the master surface. The master can be fabricated by micromachining or lithographic techniques, and the fluid precursor of the mask can be applied to the master surface by any technique such as pouring, spreading, spin-coating, and the like. Most preferably, the master is fabricated by photolithography, and a precursor of an elastomeric material is spin-coated on a surface of the master and allowed to harden, and is removed to define an elastomeric mask. The fabrication technique can involve applying different layers of fluid precursor to form a mask including several layers.

Other advantages, novel features, and objects of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings, which are schematic and which are not intended to be drawn to scale. In the figures, each identical or nearly identical component that is illustrated in various figures is represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention.

#### Brief Description of the Drawings

Fig. 1 schematically illustrates a photolithographically-prepared template for creation of an elastomeric masking system of the invention;

Fig. 2 schematically illustrates a polymeric elastomeric masking system formed on the template of Fig. 1;

Fig. 3 schematically illustrates a masking system formed as shown in Figs. 1 and 2, following removal from the template;

Fig. 4 schematically illustrates formation of an array of organic electroluminescent pixels on a surface using the masking system of Fig. 3;

Fig. 5 schematically illustrates formation of a multi-color organic electroluminescent array using a masking system of multiple masks;

5 Fig. 6 is a top view of the masking system used in the procedure of Fig. 5;

Fig. 7 schematically illustrates formation of an array of different materials on a surface using multiple masks;

Fig. 8 illustrates schematically a technique for application of a fluid to regions of a substrate surface in register with channels of a masking system as illustrated in Figs. 3-7;

10 Fig. 9 is a photocopy of a scanning electron micrograph (SEM) image of gold dots created on a substrate surface using a masking technique of the invention;

Fig. 10 is a photocopy of a SEM image of wells created using a masking system of the invention;

Fig. 11 is a photocopy of an image of electroluminescence from electroluminescent pixels created on a surface using a masking system of the invention;

Fig. 12 is a photocopy of an optical micrograph image of photoluminescent material created on a substrate surface using the masking technique of the invention; and

Fig. 13 is a photocopy of an image showing photoluminescence of photoluminescent pixels created on a substrate surface using the masking technique of the invention;

20 Fig. 14 is a photocopy of an optical image of silver circles electroplated onto gold using a masking technique of the invention;

Fig. 15 is a photocopy of an optical image of glass circles created on silicon using a masking technique of the invention;

Fig. 16 is a photocopy of a fluorescence image of fluorescently-labeled protein immobilized at discrete regions of a surface using a masking technique of the invention;

Fig. 17 is a photocopy of an elastomeric mask defining a staggered array of crosses, used in Example 8, below; and

Fig. 18 is a photocopy of an optical micrograph of a gold grid formed using the mask of Fig. 17 in two deposition steps (see Example 8).

30

#### Detailed Description of the Invention

The following documents are incorporated herein by reference. Rogers, et al., *Appl.*

*Phys. Lett.* 7, 70, (1997); Kim, et al. *Nature*, 376, August 17, 1997, 581-584; Jackman, et al., *Langmuir*, 15:8, 2973-2984; U.S. patent application serial no. 09/004,583 of Kim, et al., entitled "Method of Forming Articles Including Waveguides Via Capillary Micromolding and Microtransfer Molding", filed January 8, 1998; U.S. Patent No. 5,512,131 of Kumar, et al. (April 30, 1996); International patent application no. PCT/US96/03073 (publication WO 96/29629, June 26, 1996); International patent application no. PCT/US97/04237 (publication WO 97/34025); and International patent application no. PCT/US97/04005 (publication WO 97/33737, September 18, 1997).

The present invention provides a mask, and techniques for use of the mask that involve shielding selected portions of a surface, while leaving other portions unshielded, and allowing an agent to be applied to unshielded portions via deposition, chemical reaction, or the like. The mask can shield selected portions of the surface by being brought into contact with those portions and, in preferred embodiments, the mask has a flexible surface that allows the mask to conform to the surface. The entire mask can be flexible and therefore can conform to a non-planar surface. In particularly preferred embodiments the mask is a polymeric elastomer that can form a seal against a substrate surface. It is a feature of the invention that masks of the invention can form a seal against a substrate surface in the absence of any clamping apparatus or other apparatus used to apply a force against the mask in a direction of the substrate surface. Where elastomeric surfaces are used, and the elastomeric surface and substrate surface to be masked are clean, sealing can occur essentially instantaneously upon contact without application of significant pressure, and sealing can be maintained without maintenance of any pressure. This sealing is reversible, that is, the mask can be removed from the substrate surface by being peeled off, and can be reused on the same or a different substrate surface. Reusability of a particular mask increases with the thickness of the mask.

The mask can be used for a variety of applications, one of which is the fabrication of an array of pixels of an organic electroluminescent material on a substrate. Multi-colored, pixelated arrays can be made using the preferred mask of the invention via a technique that avoids the use of solvents during fabrication, and does not require encapsulation of pixels between formation steps. The mask can include a very small-scale pattern, for example an array of holes of less than about 1 millimeter down to less than about 1.5 micron. When the mask conforms to and seals against a substrate, material can be patterned through the holes against the substrate, and the mask removed, leaving an array of pixels, without the

requirement of steps and apparatus involved in laser ablation, photolithography, and shadow mask procedures.

Referring now to Figs. 1-3, one exemplary technique for fabricating a mask in accordance with the invention is illustrated schematically. Fig. 1 shows a master 20 for  
5 fabricating an elastomeric mask of the invention. Master 20 includes a substrate 22, on a top surface 24 of which is created an array of essentially cylindrical posts 26 via, for example, photolithography. Referring to Fig. 2, a prepolymeric material 28 then is spin-cast onto the master 20 (on surface 24 and around posts 26) such that the thickness of prepolymer layer 28 is less than the height of posts 26. Posts 26 thus protrude slightly above the layer of  
10 prepolymer material 28. After curing of the prepolymer it is peeled away from the master 20 to yield a membranous mask 30 as shown in Fig. 3. Mask 30 includes a plurality of holes, or channels 32 that correspond to posts 26 of master 20.

The pattern of channels 32 in mask 30 is for illustrative purposes only. Any pattern, for example a pattern defined by a single channel or many channels that can be circular, oval,  
15 square, rectangular, and the like, and arranged in a grid-like array (as illustrated) or in a non-array (for example random pattern) can be used. The pattern can include alphanumeric characters. The mask and channels can be of a variety of dimensions. In preferred embodiment, the mask has a thickness (which defines a channel length) of no more than about 1 millimeter. Preferably, the thickness of the mask is no more than about 500 microns, more  
20 preferably no more than about 200 microns, more preferably no more than about 100 microns, more preferably still no more than about 25 microns, and the mask can be no more than about 30 microns thick in some embodiments. The channels have a preferred cross-sectional dimension that corresponds to the thickness of the mask to create a length-to-diameter ratio of channels of no more than about 5 to 1. Preferably, the channels have a length-to-diameter  
25 ratio of no more than about 2 to 1.

The mask is particularly suited for creation of high-resolution electroluminescent displays, or other devices requiring high resolution and large numbers of small features, and accordingly in preferred embodiments includes at least about 100 channels 32. At least about  
30 50% of the channels in this embodiment have a cross-sectional dimension of less than about 200 microns. The channels can be of a variety of cross-sectional shapes and, as illustrated, are essentially circular in cross-section. Where the channels are non-circular, for example ovoid or elongated rectangular, the "cross-sectional dimension" is meant to define the shortest

distance across the cross-section of the channel. "Maximum cross-sectional dimension" in this context means the longest distance across the cross-section of the channels.

Preferably, at least about 98% of the channels 26 have a cross-sectional dimension of less than about 200 microns, more preferably the mask includes at least about 500 channels  
5 each of less than about 200 microns in cross-sectional dimension, and each channel spaced from an adjacent channel by no more than about 400 microns. This close spacing is particularly important in creation of microelectronic devices where each component created in register with a channel 32 should not be in electrical communication with an adjacent component. The mask of the invention facilitates surprisingly high-resolution deposition that  
10 allows creation of components in close proximity to each other but without contact with each other (leakage between the mask and masked surface is avoided).

In more preferred embodiments the mask can include at least about 1000 channels, 1500 channels, or even 2000 or more channels, with at least about 50% of the channels, more preferably at least about 98% of the channels, or essentially all of the channels having a cross-  
15 sectional dimension of less than about 100 microns, with each channel spaced from an adjacent channel by no more than about 200 microns. More preferred channel dimensions are less than about 50 microns, less than about 25 microns, less than about 10 microns, less than about 5 microns, less than about 3 microns, and less than about 1.5 microns, with spacing between channels of no more than about twice the cross-section of each channel. In all of the  
20 above-described embodiments, the cross-section can be maximum cross-sectional channel dimension.

One technique for use of mask 30 of the invention will now be described with reference to Fig. 4. Fig. 4 illustrates fabrication of a pixelated electroluminescent device. A substrate 34 (e.g., glass) is provided and a hole-transporting material (e.g., poly(N-vinyl  
25 carbazole) (PVK)) 36 is spin-coated onto an indium tin oxide (ITO) substrate 38 deposited on a top surface 40 of substrate 34. Mask 30 of the invention (shown in cross-section) is brought into conformal contact with top surface 42 of the hole-transporting material 36. Mask 30 can conform to surface 42 and form a close and reversible seal therewith. The tightly-sealed mask 30 allows selective deposition, through channels 32 thereof, of an emitter 44 (e.g., 8-  
30 hydroxyquinoline aluminum) via thermal evaporation to form a plurality of pixels of the emitter 44. Although not illustrated in Fig. 4 or in other figures, when a masking system is used to shield portions of a surface and deposition occurs at portions other than shielded

portions, deposition may occur atop exposed surfaces of the masking system as well. Mask 30 then is re-placed by being removed from surface 42 of hole-transporting material 36, leaving the pixels 44 of emitter intact and adhered to surface 42. As used herein, "re-place" is meant to define moving the mask in any way between steps in a deposition process. Re-place  
5 can define removing the mask from the surface completely, or re-orienting the mask at the surface, that is, removing the mask and replacing the mask at the same surface in a different position. It is a feature of the invention that the mask is cohesive and can be removed from a surface as a single unit and re-used, i.e., the mask facilitates a "dry lift-off" procedure. The mask is cohesive in that attractive forces within the mask that hold the mask together are  
10 stronger than forces typically required to remove the mask from a surface. That is, the mask can be used to seal a surface during a deposition process, then can be removed by lifting a

can be reused. This is to be distinguished from a lithographically-created mask such as a photoresist mask. Use of a cohesive mask of the invention allows formation of the mask on  
15 the surface to be masked without degrading, at the surface, portions defining channels 32 (such as are degraded in creation of a lithographically-created mask). A cathode 46 (e.g., aluminum) then is evaporated on top of the device so as to cover and surround pixels 44 and coat portions of top surface 42 of hole-transporting material 36 not covered by pixels 44. Application of an electrical potential between cathode 46 and anode 38, via an electrical  
20 circuit 48 (including a power source 50 in electrical communication with cathode 46 and anode 38) creates electroluminescence 52 emanating from pixels 44.

Referring now to Fig. 5, one technique for forming a multi-layer pixelated electroluminescent structure that can be used in accordance with the invention is illustrated schematically. The mask used in the technique illustrated represents but one pattern that can  
25 be used to pattern a surface. Other patterns, including different sizes, shapes, and spacing of channels can be used. The technique takes advantage of a method of the invention involving shielding a portion of a surface with a mask and applying an agent to an unshielded portion, then re-placing the mask and applying an agent to a shielded portion. A first mask 30 is brought into conformal contact with top surface 42 of hole-transporting material 36. Then, a  
30 second mask 300 is placed atop mask 30, the first and second masks defining a masking system. Mask 300 includes a plurality of channels 302 that are larger than channels 32 of mask 30. Mask 300 is placed atop mask 30 such that several of channels 32 of mask 30 are

shielded by mask 300, while others of channels 32 remain unshielded. Specifically, mask 300 includes a series of linear channels 302 (elongates channels that extend into and out of the page) that allow exposure of a linear array of channels 32 of mask 30 to be exposed, while shielding other linear arrays of channels 32. As illustrated, mask 300 is aligned with every  
5 third line of channel 32 of mask 30. Together, the masking system defined by masks 30 and 300 shields a first portion of surface 42. An emitter 44 then is evaporated through channels 32 that remain unshielded to create a linear array of pixels at a second portion of surface 42. Mask 30 then is re-placed, i.e., re-oriented in relation to the surface, to shield a different set of channels 32. Specifically, mask 300 is removed, re-aligned, and re-sealed so as to shield  
10 channels 32 that it had left unshielded in the step previously described, while shielding an adjacent, linear array of channels 32. A second evaporation step of a second emitter 45 creates lines of pixels of a different color emitter on a portion of the first portion (which had been shielded originally) of surface 42. This process can be repeated, exposing the remaining linear array of channels 32 to a third emitter 47. Finally, both masks 300 and 30 are re-placed  
15 (removed) leaving a linear array of pixels 44, a linear array of pixels 45 next to the array of pixels 44, and a linear array of pixels 47 in between the linear arrays 44 and 45. Where emitter pixels 45 emit red light, emitter pixels 44 emit green light, and emitter pixels 47 emit blue light, red, green, and blue light, respectively, will be emitted when an electrical potential is applied between cathode 46 (deposited atop pixels 44, 45, and 47) and anode 38 via  
20 electrical circuit 48.

Fig. 6 illustrates the technique of Fig. 5 from a top view. Mask 30 in Fig. 6 includes linear arrays 52, 54, and 56 of channels (holes) 32, corresponding to the different pixel arrays 44, 45, and 47 of Fig. 5. Mask 300 is a slit mask including an elongated opening (channel) 302, and mask 300 is positioned atop mask 30 such that channel 302 leaves linear array 56 of  
25 channels 32 of mask 30 unshielded, while shielding linear arrays 52 and 54 of channels 32. Mask 30 seals against top surface 42 of hole-transporting material 36 (not shown) and mask 300 seals against mask 30 after deposition of a first emitter material 44 in channels 32 of array 54. Mask 300 then is re-placed so as to expose array 54 of channel 32, while sealing against mask 30 so as to shield arrays 52 and 54. A second emitter material 45 then is deposited in  
30 channels of array 56, mask 300 then is re-placed so as to expose array 52 while shielding arrays 54 and 56, and a third emitter material 47 is deposited in channels 32 of array 52. Both masks then are re-placed (removed). The technique illustrated in Figs. 5 and 6 can be carried

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out by hand under a stereoscope at resolution of about 200 microns, and at higher resolution using a rotation and alignment stage apparatus of the type readily available and usable by those of ordinary skill in the art.

Fig. 7 illustrates a technique similar to that illustrated in Figs. 5 and 6, where a  
5 masking system including multiple masks is used and individual masks are re-placed not by being re-oriented relative to a substrate surface, but being removed between deposition steps. The arrangement in Fig. 7 involves selective deposition of a variety of materials on a surface  
70 of a substrate 72. Masks 30, 300 and 310 are stacked, in that order, on a surface 70. Mask 30 includes a plurality of channels 32, mask 300 includes a plurality of channels 302, and  
10 mask 310 includes a plurality of channels 312. The masks are in register with each other such that in some cases channels of all three mask are in register with each other, in other cases

mask is not in register with any channel of any other masks. As illustrated, this results in an arrangement in which every third channel 32 of mask 30 is in register with channels 302 and  
15 312, every third channel 32 is in register with channel 302 only, and every third channel 32 is in register with no other channel. Following arrangement of the masks in this manner on surface 70 to shield a first portion of surface 70, the surface is exposed to conditions allowing deposition of a first agent 314 on a second portion of surface 70. Agent 314 is deposited only at those regions in which channels 32, 302, and 312 of masks 30, 300, and 310, respectively,  
20 are in alignment. Following removal of the top mask 310, a portion of the first portion of surface 70, that is, regions in which channels 32 and 302 had been in alignment, but not in alignment with any channel 312 of mask 310, now are exposed for further deposition. Exposure of the surface to appropriate conditions results in deposition of agent 316 atop agent 314 (under conditions where agent 316 can be deposited atop agent 314) as well as deposition  
25 at regions in which channels 302 and 32 had been in alignment but shielded by mask 310. Following removal of mask 300, additional regions of the first portion of surface 70 in register with channels 32 of mask 30, that had not been in register with channels of either of masks 300 and 310, experience deposition of agent 318 under exposure to appropriate conditions. Agent 318 also is deposited atop agents 314 and 316, where those agents are exposed, under  
30 conditions appropriate for such deposition. This technique can find use where it is desirable to expose, upwardly, different agents 314, 316, and 318. Where this is desired, the technique illustrated in either of Fig. 7 or in Figs 5 and 6 can be used. The technique of Fig. 7 is useful,



in addition, where it is desired to have multi-layered structures for electronic or other purposes as would be apparent to those of ordinary skill in the art.

Mask 30 is used to shield portions of a surface not in register with channels 32 from an agent. In all of the embodiments described herein, shielding can be accomplished by positioning mask 30 proximate to a surface (such as surface 42 of material 36). "Proximate" in this context can define contact, or can define positioning of the mask between a source of the agent and the surface upon which the agent is to be patterned. Preferably, mask 30 is brought into contact with the surface desirably patterned and it is a feature of the invention that the surface of mask 30 that is brought into the surface of the article to be patterned is flexible so that it can be brought into conformal contact with the surface of the article to be patterned. "Conformal contact" in this context is meant to define essentially continuous contact between portions of mask 30, other than channels 32, and the surface of the article to be patterned. This is to be distinguished from, for example, a metal screen or a rigid polymer, each of which can contact a surface to be masked but which are not flexible enough to conformally contact the surface. In particularly preferred embodiments, a surface of mask 30 seals against a surface of an article to be patterned. "Seal" in this context means that when the mask is sealingly engaged with a surface and a fluid is applied to the masked surface, the fluid is allowed to contact only those portions of the masked surface in register with channels 32 of the mask and the fluid does not pass under the mask and contact shielded portions of the article surface covered by solid portions of the mask, so long as the fluid does not degrade the mask or the surface to be patterned (in which case fluid could pass under the mask due to degradation of the mask and/or surface). "Sealing" in this context is to be distinguished from the operation of other rigid or flexible masks that may be brought into conformal contact with a surface, but that can not seal against the surface.

Preferably, the surface of mask 30 that is brought into contact with a surface to be masked is flexible and polymeric, and preferably the entire mask 30 is flexible and polymeric. In particularly preferred embodiments, the surface of mask 30 used to mask a surface of an article is elastomeric, which allows the mask to readily seal the article to be masked, and in particularly preferred embodiments the entire mask 30 is elastomeric. As used herein, "elastomeric" defines an elastic polymer. Where mask 30 is flexible or elastomeric in its entirety, the masking of non-planar surfaces is facilitated. "Non-planar" includes curved surfaces. The mask of the invention can readily conform to surfaces having relatively small

radii of curvature. For example, masks of the invention can be used to pattern agents on surfaces having both negative and positive radii of curvature, such as both concave and convex surfaces. Masks of the invention have been used to pattern agents on the interior and exterior of cylindrical substrates.

5 Article 30 can be fabricated of an elastomer as described in co-pending, commonly-owned U.S. Patent No. 5,512,131, issued April 30, 1996 by Kumar, et al, entitled "*Formation of Microstamped Patterns on Surfaces and Derivative Articles*", and as described in International Patent Publication No. WO 96/29629 of Whitesides, et al., entitled "*Microcontact Printing on Surfaces and Derivative Articles*", published June 26, 1996, both  
10 of which are incorporated herein by reference. One useful technique for fabricating article 30 involves spin coating an elastomer on a master (described above with reference to Fig. 1)

et. al. This allows for even application of a layer of defined thickness thinner than the height of features on the surface of the master that create channels in the mask.

15 Elastomeric surfaces and masks of the invention should have a Shore A hardness of preferably from about 30 to about 70, so long as the elastomer can provide a seal where desired. Exemplary elastomers are disclosed in U.S. Patent No. 5,691,018 (Kelley et al., filed December 15, 1995), incorporated herein by reference.

Substrates that can be masked and patterned using mask 30 of the invention can be  
20 essentially any material including polymers, metals, ceramics, oxides, and the like. Silicon and silicon dioxide can be patterned using mask 30.

Any of a wide variety of agents can be applied to portions of an article of a surface remaining unshielded (in register with channels 32) by mask 30. Many of these are "dry" processes, and others involve "wet" chemical processing. The agent can be a precursor of a  
25 chemical vapor deposition product, that is, an article can be masked using mask 30 and exposed to chemical vapor deposition conditions whereupon a product, defining the agent, is deposited in unshielded portions in register with channels 32. Other "dry" processes include reactive ion etching or thermal or e-beam evaporation or sputtering of metals, metal oxides, and ceramics. Metal deposition, such as "wet" electrochemical deposition or electroless  
30 deposition, can be carried out from fluid precursors defining electrochemical or electroless plating baths. A prepolymeric fluid precursor can be used, such as a fluid containing species that can react to form a thermoset polymer at unshielded portions, or a fluid pre-polymer that

can be polymerized at unshielded portions via photolysis, convective or radiative heat, free-radical polymerization, and the like. Additionally, a relatively low-melting polymer can be applied in a molten form, allowed to solidify at unshielded portions, followed by removal of the mask. These and other forms of polymerization are known to those of ordinary skill in the art and can be applied to the techniques of the present invention without undue experimentation. All types of polymerization, including cationic, anionic, copolymerization, chain copolymerization, cross-linking, and the like can be employed, and essentially any type of polymer or copolymer formable from a fluid precursor can be patterned in accordance with the invention. An exemplary, non-limiting list of polymers that are suitable include

polyurethane, polyamides, polycarbonates, polyacetylenes and polydiacetylenes, polyphosphazenes, polysiloxanes, polyolefins, polyesters, polyethers, poly(ether ketones), poly(alkylene oxides), poly(ethylene terephthalate), poly(methyl methacrylate), polystyrene, and derivatives and block, random, radial, linear, or teleblock copolymers, cross-linkable materials such as proteinaceous material and/or blends of the above. Gels are suitable where dimensionally stable enough to maintain structural integrity upon removal of mask from the substrate surface. Also suitable are polymers formed from monomeric alkyl acrylates, alkyl methacrylates, alpha-methylstyrene, vinyl chloride and other halogen-containing monomers, maleic anhydride, acrylic acid, acrylonitrile, specifically, methyl methacrylate, imides, carbonates, hexafluoroisopropyl methacrylate, acrylonitrile, bromophenyl acrylates or bromophenyl methacrylates, and the like. Monomers can be used alone, or mixtures of different monomers can be used to form homopolymers and copolymers. Non-linear and ferroelectric polymers can be advantageous. The particular polymer, copolymer, blend, or gel selected is not critical to the invention, and those of skill in the art can tailor a particular material for any of a wide variety of applications.

A variety of organic electroluminescent materials can be used, including those described in the following articles, each incorporated herein by reference: Renak, et al., "Microlithographic Process for Patterning Conjugated Emissive Polymers", *Adv. Mater.*, 1997, 9, 5, 392-394; Yam, "Plastics Get Wired", *Scientific American*, July 1995, 83-87; Kijima, et al., "RGB Luminescence from Passive-Matrix Organic LED's", *IEEE Transactions on Electron Devices*, 44, 8, August 1997; Shen, et al., "Three-Color, Tunable, Organic Light-Emitting Devices", *Science*, 6, June 27, 1997; Burrows, et al., "Achieving Full-Color Organic Light-Emitting Devices for Lightweight Flat-Panel Displays", *IEEE Transactions on Electron*

*Devices*, 44, 8, August 1992.

According to one embodiment, a polymerizable or cross-linkable species (optionally in a fluid carrier) including an admixed biochemically active agent such as a protein can be made to form a pattern on a substrate surface according to the described technique. For example, 5 carboxylated Dextran™ can carry admixed protein, be introduced into channels 32, and hardened. Where the Dextran™ carries admixed biologically active agent, the article can be exposed to a medium suspected of containing a biological binding partner of the biochemical agent, and any biochemical binding or other interaction detected via, for example, diffraction, or via a change in coupling between waveguide cores as described more fully below.

10 According to another embodiment, a species such as polymerizable or cross-linkable species can entirely coat a surface, mask 30 can be placed adjacent the surface, a biological agent can

~~be introduced into channels 32, and the species can be polymerized or cross-linked.~~

species, and prior to or subsequent to removal of mask 30 species on the surface can be polymerized or cross-linked. In this manner, a surface having a pattern of biological agent 15 compounded therein is produced, and can serve as a sensor for a biological binding partner of the biological agent via change in refraction or diffraction of light at the surface.

According to one embodiment of the invention, a patterned article is created using mask 30 that is dissolved or dispersed in a fluid carrier to form fluid precursor which is introduced into channels 32, whereupon the fluid carrier or solvent dissipates (e.g., is 20 removed via evaporation from the mold channels and/or absorption into the substrate or mask 20). According to yet another embodiment, a patterned structure erected is an inorganic structure, such as a salt or ceramic. A salt soluble in a fluid precursor can be prepared as a solution defining a fluid precursor that is introduced into channels 32 and precipitated as a patterned salt structure by removal of solvent via evaporation, adsorption, or other physical or 25 chemical change to the surrounding environment. Inorganic salts or ceramics can be carried as a suspension in a fluid carrier, flowed into channels 32, and precipitated or deposited. Metals, such as those commonly deposited from pastes in accordance with thick-film silk-screening techniques, can be applied to regions of a substrate surface defined by channels 32 where a paste is sufficiently fluid, or the paste and/or metal can be carried in a fluid as a 30 suspension or sol in a fluid precursor. Those of ordinary skill in the art will recognize that a wide variety of non-electrically conductive, electrically semi-conductive, and electrically-conductive structures can be patterned proximate a substrate surface according to the

inventive technique. Fluid precursors of inorganic materials, such as solutions from which materials can be precipitated, or suspensions from which a fluid carrier can be removed by dissipation or evaporation, can be used to form structures, such as waveguides, from materials such as  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{SiO}_2$ ,  $\text{ZnO}$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{HfO}_2$ ,  $\text{ZrO}_2$ , or the like. U.S. Patent Nos. 5,009,483, 5,369,722, and 5,009,483, each incorporated herein by reference, describe many suitable precursor and waveguide materials. Dye-doped fluid precursors can be used, and are advantageous in many situations.

Another fluid precursor can be a sol-gel precursor, and sol-gel techniques known to those of skill in the art can be used to create the solid structures in patterns, according to the invention. Ferroelectric and electrooptic materials and sol-gel processing of a variety of precursors to form a variety of species is well known to those of ordinary skill in the art and can be applied and exploited by the method of the invention. For example, materials such as  $\text{PbScTaO}_3$ ,  $(\text{Pb}, \text{La})\text{TiO}_3$  (PLT),  $\text{LiNbO}_3$ ,  $\text{KNbO}_3$ ,  $\text{LiTaO}_3$ , potassium diphosphate, potassium triphosphate,  $\text{PbMoO}_4$ ,  $\text{TeO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{BaTiO}_3$ , BBO crystals,  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ,  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ ,  $\text{SrTiO}_3$ , bismuth strontium tantalate, and the like. Other examples of sol-gel precursors that can define fluid precursors of the invention include precursors of multicomponent glasses or ceramics containing at least one oxide, such as silicate glasses or ceramics containing the oxides of aluminum, boron, phosphorus, titanium, zirconium, sodium, etc... Other sol-gel precursors appropriate for use are precursors of hybrid materials or organically modified ceramics, such as precursors of silicon oxycarbide or ORMOCERs. Other sol-gel precursors appropriate for use are described by Brinker and Scherer, in *Sol-Gel Science*; Academic Press, San Diego, 1990; Dislich, *Transformation of Organometallics into Common and Exotic Materials*; Nijhof, Dordrecht, 1998, volume 141; Pani, et al., *J. Am. Ceram. Assoc.*, 1994, 77, 1242; Ramamurthi, et al., *Mat. Res. Soc. Symp. Proc.*, 1992, 271, 351; Peiying, et al., *Sensors and Actuators*, 1995, A49, 187; Rao, *J. Electrochem. Soc.*, 1996, 143, 189; Li, et al., *Solar Energy Materials and Solar Cells*, 1995, 39, 179, each of which is incorporated herein by reference. Where a sol-gel precursor is used, a hydrolysis and polycondensation reaction takes place, preferably a two-step reaction. The working examples described herein use tetramethylorthosilicate as the main constituent in glasses formed according to this reaction. Other alkoxides react similarly. Sol-gel precursors that include mixtures of glasses or glasses that are mixtures of compounds. These structures can be deposited in any pattern that corresponds to a pattern defined by channels 32 and can include dimensions through a wide

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range as described herein. According to yet another embodiment, a biologically active agent can be dissolved or suspended in a fluid carrier as a fluid precursor and introduced into channels 32 adjacent portions of a surface masked with mask 30 and, prior or subsequent to removal of the mask, allowed to engage in a biochemical interaction proximate regions of substrate the surface in register with channels 32. For example, a biochemical agent can include a biotin linker while the substrate surface carries immobilized avidin, and biochemical interaction can be allowed to take place at regions of substrate the surface in register with channels 32 in this manner, linking the biochemical agent to the substrate surface at those regions. Biochemical agents can be immobilized proximate regions of the substrate surface according to other techniques as well. For example, where a substrate surface exposes a hydrophobic functionality, a biological agent such as a protein can be non-covalently

orientation of a protein or other biochemical agent immobilized at a substrate surface via hydrophobic interaction, a hydrophobic chemical moiety can be coupled to the biochemical agent at a region of the agent remote from its active site. In this manner, the agent can be hydrophobically coupled to the surface and maintain exposure, away from the surface, of its biochemically active region. One of ordinary skill in the art can conduct a simple test to determine whether a biochemical agent is suitable for use with the described technique. The binding constant of a candidate biochemical agent for a target species can be determined using standard ELISA techniques. Then, the candidate biochemical agent can be hydrophobically immobilized (or immobilized in any other manner described herein or known to those of ordinary skill in the art, for example via a polyamino acid tag coupled to a metal ion immobilized at the surface by a chelating agent) at a variety of surfaces, and then assays can be performed to determine whether the agent has retained its ability to biologically bind to the target species or has been denatured and is unable to bind (this exemplary test is particularly useful in connection with biological agents that, in their native form only, bind target species, but when denatured do not bind the target species).

Biochemical recognition can be exploited in immobilization of a particular biochemical agent desirably patterned on a substrate surface. For example, a first agent can be immobilized (for example using hydrophobic coupling) at regions of the substrate surface (in register with channels 32), and a second agent (which is a biological binding partner of the first agent) then can be immobilized at regions other than those regions (for example via the

technique illustrated in Figs. 5-7). Biochemical recognition involving partners also can be exploited to trap biological agents at regions of the substrate surface using other biological agents that have been immobilized at those regions via mask 30. Biochemical recognition involving partners such as antibody/antigen, antibody/hapten, enzyme/substrate, enzyme/inhibitor, enzyme/cofactor, biotin/avidin, binding protein/substrate, carrier protein/substrate, lectin/carbohydrate, receptor/hormone, receptor/effector, complementary strands of nucleic acid, repressor/inducer, and the like can be exploited in connection with the technique. Those of ordinary skill will recognize a variety of uses for placement of such biochemically active agents at predetermined portions of a substrate surface in a pattern, for example as disclosed in co-pending, commonly-owned U.S. Patent No. 5,512,131 of Kumar, et al. and International Patent Application Publication No. WO 96/29629, both referenced above.

According to yet another embodiment, a fluid precursor applied to a surface through channels 32 of mask 30 to form an agent at unshielded portions of the surface and register with channels 32 carries a suspended or dissolved chemically active agent that is an activating agent as described in a co-pending, commonly owned U.S. application serial no. 08/616,692 of Hidber, et al. entitled "Microcontact Printing of Catalytic Colloids", and corresponding international patent publication WO 97/34025, both incorporated herein by reference. When a fluid carrier is used in this and other embodiments, it can form part of a species or article immobilized proximate the substrate surface or can dissipate, for example via evaporation or adsorption into the mask or substrate surface, leaving the species carried in the fluid carrier immobilized at the surface. A non-limiting list of chemically active agents that can be patterned on a surface in accordance with the invention also includes agents as described by Lando (U.S. Patent Nos. 3,873,359; 3,873,360; and 3,900,614) which can render a substrate surface amenable to metal plating, catalytic activating agents such as finely distributed metal particles and clusters such as conventional metal powders, substrate-fixed metal clusters or multimetallic clusters that are well known as valuable heterogeneous and homogeneous catalysts in organic chemistry, inorganic chemistry, and electrochemistry, etc. With reference to the application of Hidber, et al., such agents can include those capable of being applied to unshielded portions of a surface through channels of a mask of the invention in a form in which it can effect a chemical reaction (such as a metal deposition reaction), and immobilized at the surface with a degree of adhesion and for a period of time sufficient to participate in the

desired chemical reaction. In one embodiment the chemically active agent can participate in a desired chemical reaction with the mask in position at the surface. In another embodiment, the chemically activation can be deposited at the surface in desired regions using the mask, followed by removal of the mask, followed by a second step involving the chemically activate agent. For example, a catalyst can be deposited in desired regions using mask 30, mask 30 can be removed, and the catalytically active regions of the surface (locations where channels 32 had been) can promote metal deposition at those regions selectively. As such, one class of activating agents provided in accordance with one embodiment of the invention are distinguished from prior art agents applied with an applicator such as a stamp, for example as disclosed by Lando (U.S. Patent Nos. 3,873,359, 3,873,360, and 3,900,614), in that the activating agent of the present invention is in a form suitable for effecting reaction such as

embodiments, further chemical reaction at the surface to convert a precursor to a suitable agent, as necessitated in the referenced prior art methods, is not required. Metal deposition reactions contemplated include electrochemical deposition and electroless deposition, generally involving reduction of a metal cation to create the metal, facilitated in part by the lowering of the electrochemical potential involved in the deposition.

Activating agents that are finely distributed metal particles and clusters, such as conventional metal powders, including substrate-fixed metal clusters or multimetallic clusters are suitable for use as activating agents in accordance with the invention, and are well known as valuable heterogeneous and homogeneous catalysts in organic, inorganic, and electrochemistry. Exemplary activating agents include one or more metals of periodic table groups Ib, IIb, III, IV, V, VI, VIIb, VIII, lanthanides, and actinides, preferably copper and any metal more noble than copper, in particular Pd, Au, Ag, Pt, and Cu. Hydrogenation catalysts for example those effective in hydrogenating olefins or aromatics, as in the partial hydrogenation of benzene to form cyclohexene, with a substrate-fixed ruthenium activating agent or bimetallic activating agent (e.g. Ru/Sn) are contemplated. Zirconium and titanium catalysts, among others, are suitable for use in the invention that catalyze polymerization, such as polymerization of olefins such as ethylene, and these are intended to form part of the invention. Other examples of catalytic activating agents include those used in Heck reactions, e.g. in the Pd-catalyzed reaction of bromobenzene and styrene to form stilbene. Activating agents that are heterogeneous catalysts are also useful as electrocatalysts in fuel cells (in



particular substrate-fixed Pt and Pt/Ru clusters). Activating agents prepared according to the invention can be homogeneous catalysts, such as those used in two phase systems (for instance H<sub>2</sub>O/toluene), such as e.g. betaine-stabilized Pd clusters soluble in H<sub>2</sub>O. Activating agents that are embedded in polymers can be used to prepare materials for electronic, optical and magnetic applications. Suitable embedding polymers include organic polymers, such as poly-p-phenylene-vinylene, polymethyl methacrylate, polysilanes, and polystyrene, or inorganic polymers, such as zeolites, silicates, and metal oxides. The well-known sol-gel process can be used to incorporate metal clusters in amorphous metal oxide materials (e.g. SiO<sub>2</sub>) as activating agents.

Soluble metal clusters that are activating agents can also be surface-deposited to prepare novel materials for applications in optics and electronics, e.g. Pd on HOPG (highly oriented pyrolytic graphite).

Especially preferred as activating agents in accordance with this embodiment of the invention are colloidal activating agents. Suitable colloid-forming species and colloids are described in Hidber, et al., referenced above, and in European patent publication no. 672765 by Reetz et al., published September 20, 1995, and incorporated herein by reference.

According to yet another embodiment of the invention a suspension of particulate species in a fluid carrier can be introduced into channels 32, followed by removal of the fluid carrier via dissipation, as discussed. The particulate species can be organic, inorganic, or polymeric material as described above, for example finely-ground polymeric, ceramic, or crystalline material, or can be in the form of microspheres. The application of microspheres in a predetermined pattern to a substrate surface can serve a variety of purposes that will be apparent to those of ordinary skill in the art upon reading the present disclosure, in light of the state of the art as set forth in several publications. An article by Lenzmann, et al., entitled "Thin-Film Micropatterning Using Polymer Microspheres", *Chem. Mater.*, 6, 156-159 (1994), incorporated herein by reference, describes formation of densely-packed monolayers of monodisperse polystyrene microspheres deposited on a glass substrate. The spheres serve as a mask for zinc sulfide deposition on the substrate as a thin film by thermal evaporation in vacuum. The mask (microspheres) are removed from the substrate surface after evaporative deposition leaving behind a surface with zinc sulfide features located in the interstitial spaces of the densely-packed spheres. For 2-micron diameter spheres, the lattice spacing of the resulting pattern is approximately 900 nanometers with individual trigonal pyramidal peaks.

According to the present invention, a particular concentration of polymeric microspheres in a fluid carrier can be selected without undue experimentation that, when introduced into channels 32, followed by evaporation of the fluid carrier, would result in microspheres selectively patterned at regions of a substrate surface in register with channels 32.

5 Other materials that can be patterned on a substrate surface using masks of the invention include hydrogels, via dewetting; organometallic compounds, via evaporation; and the like.

The material defining the mask of the invention should be selected, in conjunction with an agent applied to unmasked portions of a surface, or a fluid carrier of the agent, such  
10 that the mask is not adversely affected during deposition. For example, in most embodiments it is desirable that the size of channels of the mask does not change during deposition. In this case, it is advantageous to select a mask material of the mask.

A technique now will be described that can facilitate application of an agent to  
15 exposed regions of a surface of an article in register with channels of a mask of the invention. This technique makes the process feasible where, in some cases, the process would be very difficult or impossible, such as conditions in which the channels of the mask are very, very small and it is desirable to apply an agent to regions of the surface and register with the channel from a fluid that is difficult to interject into the channels. For example, where it is  
20 desirable to isolate and manipulate small quantities of liquid for studying single molecules, or very small numbers of molecules, the technique is useful. The technique can be used to position, at separate, isolated regions of a substrate surface in register with channels of a mask, less than about  $1 \times 10^5$  molecules, on average (the average number of molecules per channel), or less than about  $1 \times 10^4$  molecules or less than about 1000 molecules, or 100  
25 molecules, or 10 molecules, or even on average 1 molecule per region. This can be accomplished readily because the volume of a "microwell", defined by a channel of a mask and the portion of a surface of an article and register with the channel, can readily be determined and the concentration of molecules within a fluid introduced into such channels can be known. It is known, for example, that a 1 femtoliter vessel filled with a 1 nanomolar  
30 solution will contain, on average, 1 molecule. The use of small amounts of materials in chemical reactions limits their hazard and environmental impact, and the present invention facilitates placement of small amounts of molecules at desired regions of a substrate surface.

The present invention allows formation of an agent, or product of an agent, selectively at a surface at regions in register with a channel or channels of a masking system with particularly good edge resolution. Preferred edge resolution values listed below can be achieved in combination with other aspects of the invention, for example feature size (channel size), channel spacing, and the like. In particular, edge resolution of better than 500 nanometers can be achieved, more preferably better than 300 nanometers more preferably better than 200 nanometers, and more preferably still better than 100 nanometers. "Edge resolution" in this context, means that the edge of an agent formed at a surface, using a masking system of the invention, followed by removal of the masking system where the agents remains at the surface in the shape of the channel, deviates from the edge of the channel used to create the agent by no more of about 500 nanometers or more preferred values. That is, where a channel of a perfect square shape is used to form an agent at a surface of an article, the edges of the square agent deviate from a perfect line by no more than about 500 nanometers or more preferred ranges. Where a perfectly circular channel in a masking system is used, a resulting circular agent is deposited at a surface of a substrate where the periphery of the circle of the agent differs from a perfect circle by no more than about 500 nanometers or more preferred ranges. Of course, not all channels will be perfectly square, circular, or of other specific geometric shape, but will be of a variety of shapes for a variety of purposes. Edge resolution of an agent created using such a channel defines deviation from the shape defined by the channel.

One process for filling channels involves "discontinuous dewetting" which takes advantage of the difference in interfacial free energies of the channels and substrate surface, and the liquid that desirably fills microwells defined thereby (Jackman, et al., *Anal. Chem.* 1998, 70, 2280-7). In this technique, liquid is allowed to drain off of an array of microwells defined by mask channels and a substrate surface either by gravity or by pulling the array from a bulk solution. Where a suitable liquid/mask/substrate surface combination is selected, the microwells will remain filled with approximately equal volumes of fluid as the fluid dewets the surface of the material. Fig. 8 illustrates schematically discontinuous dewetting. In the technique, microwells 80, each defined by interior surfaces of channels 32 of mask 30 and portions of a surface of a substrate 82 in register with the channels, are filled with a fluid 84 as the substrate/mask assembly is pulled upwardly, in a vertical orientation, from a container containing fluid 84. The technique illustrated schematically in Fig. 8 is successful

where three criteria are met. First, the fluid that is to fill the microwells should not swell the material defining the mask (many non-polar organic liquids, e.g. haptene, toluene, methylene chloride, acetone, and others swell PDMS). Second, the fluid should have a low viscosity (preferably less than about 500 cps) so that it begins to dewet the surface on a reasonable time scale. Third, the fluid must have a receding contact angle on the substrate (interior surfaces of channels 32 and regions 80 of the surface of substrate 82 and register therewith) that falls in an appropriate range. Specifically, where a PDMS stamp is used and a surface of substrate 82 has similar hydrophobicity or hydrophilicity, fluids that have receding contact angles that fall between about 16° and about 81° will fill the microwells easily by discontinuous dewetting. Liquids with contact angles above 81° tend to bead on the substrate (PDMS) and do not spread to fill the wells. Where a PDMS mask is used, table 1 presents a set of liquids that will

energies and contact angles on PDMS.

15

TABLE 1

20

25

30

|                      | $\gamma_{lv}$<br>(dyn/cm) | $\theta_a$<br>(° ± 5°) | $\theta_r$<br>(° ± 5°) |
|----------------------|---------------------------|------------------------|------------------------|
| Water                | 73.0                      | 108                    | 81                     |
| glycerol             | 63.4                      | 104                    | 70                     |
| ethylene glycol      | 48.0                      | 92                     | 54                     |
| tri(ethylene glycol) | 45.6                      | 76                     | 59                     |
| dimethylsulfoxide    | 43.5                      | 88                     | 40                     |
| dimethylformamide    | 37.0                      | 63                     | 35                     |
| butanol              | 24.6                      | 36 <sup>a</sup>        | 16 <sup>a</sup>        |
| ethanol              | 22.4                      | 31 <sup>a</sup>        | 20 <sup>a</sup>        |
| perfluorodecalin     | 18.3                      | 36 <sup>a</sup>        | 27 <sup>a</sup>        |

Where a volatile fluid is used to fill the microwells, problems associated with rapid

evaporation of the fluids can be experienced unless steps are taken to counteract evaporation. Such steps can include the use of high ionic strength, buffered, aqueous solutions (where aqueous solutions are desired, for example, for biological experiments), and closed, humidity-controlled environments. Evaporation problems can be avoided completely by using less volatile solvents or co-solvents (e.g., triethyleneglycol).

Individual microwells also can be addressed with different fluids using a sharp glass probe (approximately 15 microns in diameter) that was used to hold a drop of fluid and to drag the drop of fluid across an array of microwells, filling a single line of microwells selectively. One probe can be made by dipping an optical fiber (125 microns diameter) into 48% HF for about 10 minutes. Individual wells can be selectively addressed in this manner by mounting a probe on an XYZ stage.

Described above are techniques in which a masking system is positioned adjacent a surface of an article, an agent is applied through a channel in the masking system to a surface of the article, and the masking system is re-placed followed by further application of an agent to a surface of the article. As described, this can involve moving, or re-orienting a mask on a surface so that channels in the mask align with different portions of the surface, and reapplication of an agent, or application of a new agent, through channels in the mask. This can be used to create continuous, or connected patterns on a surface using a mask with discontinuous, or non-connected channels, and this can have particular use in the microelectronics industry. In Example 8, below, a technique is described in which a single mask is used in two steps to direct a patterned array of isolated features in a first step, followed by re-orientation of the mask at the surface to produce the same pattern at the surface, but shifted laterally, the second pattern connecting the isolated regions defined by the first pattern to form an overall connected pattern. The resulting pattern, as illustrated in Fig. 18, is a grid pattern that would have been impossible to produce using a single mask deposition step because it would have required the mask to contain a series of disconnected squares.

The function and advantage of these and other embodiments of the present invention will be more fully understood from the examples below. The following examples are intended to illustrate the benefits of the present invention, but do not exemplify the full scope of the invention.

#### Example 1: Fabrication of a Mask

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A polydimethylsiloxane (PDMS) mask was fabricated.

A master (Fig. 1) including an array of photoresist posts on a silicon wafer was created by photolithography. The master consisted of an array of features in photoresist created on a silicon wafer. It was generated either by "rapid prototyping" (for feature sizes  $> 50 \mu\text{m}$ ) - by  
5 using a high-resolution transparency as the photomask for photolithography - or by performing standard photolithography with a chrome mask (for feature sizes  $< 50 \mu\text{m}$ ). The photomasks for performing photolithography were either rigid chrome masks (Advanced Reproductions, North Andover, MA; features  $< 50 \mu\text{m}$ ) or transparencies (produced using Herkules PRO image setter, 3387 dpi, Linotype-Hell Co., Hauppauge, NY, by a desktop  
10 publishing company, Pageworks, Cambridge St., Cambridge, MA; features  $> 50 \mu\text{m}$ ). In standard photolithography techniques, SU-8 50 (SU-8 5) resist (as received from

rpm for 40 s (2500 rpm for 40 s) produced a film approximately  $50 \mu\text{m}$  thick. After baking the resist at  $105^\circ\text{C}$  for 15 min. (5 min), it was exposed to UV light for 1 min (10 s) through a  
15 mask using a Karl Suss mask aligner. Features were developed in propylene glycol methyl ether acetate (PGMEA) for ~5 min (1 min) after the wafer had been baked for 15 min (5 min) at  $105^\circ\text{C}$ .

Surface treatment of the silicon wafer by exposure to the vapor of perfluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (United Chemical Technology, Bristol, PA) in a vacuum  
20 desiccator prevented adhesion of the elastomer to the wafer during the next step. Posts with diameters between 50 and 500 microns were 50 microns thick; for smaller (1.5 to 50 micron diameter) posts, the thickness of photoresist was approximately equal to the diameter of the posts.

Sylgard 184 silicone elastomer, parts A and B (10:1, by weight, Dow Corning) were  
25 mixed in a container and trapped air was removed under vacuum. PDMS was spin-coated onto the master so that the thickness of the layer of polymer was less than the height of the posts of photoresist. For 50 micron thick posts, the elastomer mixture was spin-coated at 3000 rpm for 40 s to yield a 30 micron layer of polymer; for thinner posts, the elastomer mixture was diluted in toluene and then spin-coated at 3000 rpm for 60 s. The PDMS was  
30 cured at  $65^\circ\text{C}$  for one hour. Especially in the case of thinner masks (less than 50 microns thick) a 1-mm thick layer of elastomer mixture was then painted around the pattern and cured. The polymer was peeled away from the master, using the thicker surround of PDMS as a

support (in the case of the thinner masks), to yield a flexible, elastomeric membranous mask containing an array of holes with diameters varying from 1.5 to 500 microns.

Several factors determined the thicknesses of the elastomeric masks formed by this technique: speed and duration of spin-coating; lateral dimensions and spacing of features on the master; and the viscosity of the prepolymer (which changes as a function of time). For a given master (50 micron diameter circles, spaced by 50 microns) a given spin speed (3000 rpm) and PDMS mixed and degassed in vacuo for approximately 20 minutes before spin-coating, the mask thickness varied between 26 and 53 microns (at a minimum, i.e., between a set of four holes; and between 45 and 55 microns in the regions immediately adjacent to each feature) for different periods of spin-coating. When spin-coating for periods less than 50 seconds, the thickness of the mask was greater than the height of the features of photoresist on the master: the film of PDMS contained no holes. Spin-coating for more than 160 seconds resulted in defects in the masks that were significantly larger than the features. For times between 50 and 160 seconds, the masks were self-supporting and contained open holes. We typically used masks at the thicker end of this range to facilitate handling.

It is helpful in some circumstances, when using masks of the invention, to place a drop of fluid such as (in the case of a PDMS mask), 2-propanol or ethanol onto the mask after bringing it into contact with a substrate to reduce the tendency of the mask to stick to itself. Alternatively, to lessen self-adhesion, a second layer of a non-elastomeric polymer could be added to the elastomeric mask by spin-coating, for example, a layer of epoxy onto PDMS before its removal from the master. The composite mask did not tend to stick to itself, but still maintained its ability to seal against both planar and nonplanar surfaces.

To make two-layer masks (with PDMS and epoxy layers), supporting border of PDMS around the features was not formed; instead, after curing the PDMS, its surface was oxidized for 30 s using a plasma cleaner (Harrick, PDC-23G) and then a layer of epoxy (~10  $\mu\text{m}$  thick; Eporek UVO114, Epoxy Technology, Billerica, MA) was spin-coated (800 rpm for 35 s) onto the wafer. Exposure to UV light for ~10 min cured the layer of epoxy. Rigid borders were produced around these masks by dispensing epoxy from a syringe to form a supporting frame around the features. Further exposure to UV light for ~10 min hardened the second layer of epoxy.

To release the masks, a cut was made around the border with a scalpel and then, using a pair of tweezers, the mask was peeled slowly from the master. The masks were brought into

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contact with the substrate to be patterned using a pair of tweezers. On contact with the substrate, the mask wet the surface and formed a reversible seal with it. If the mask was not lying flat on the substrate to begin, the mask was removed with tweezers, replaced on the surface, and allowed to reseal. In cases when using solvents was not problematic, a drop of 2-propanol was often placed on a mask in contact with a substrate. This procedure made it easier to ensure that the mask was lying flat on the substrate. In the cases where registration of the mask to an existing pattern was required, the sealing steps were performed under a stereoscope (Wild M26 stereoscope, Leica, Heidelberg, Germany) using a set of translation and rotation stages (Newport Corp., Irvine, CA).

10 Example 2: A "Dry" Lift-Off Method: (A) Deposition of Agent Through Channels of Mask Followed by Removal of the Mask

patterned structure adhered to a substrate. A surface of the mask of Example 1 was sealed against a silicon substrate surface. The masked surface was exposed to conditions of gold e-beam deposition, resulting in deposition of gold on surfaces of the silicon substrate in register with channels of the mask. Specifically, deposition of a thin layer of titanium (5 nm, ~0.1 nm/s) followed by a layer of gold (50 nm, ~0.3 nm/s) by electron-beam evaporation (based pressure  $\sim 5 \times 10^{-7}$  Torr) onto the masked substrate resulted in metal on both the substrate and the mask. Instead of processing with solvents to remove the "mask" of photoresist as in conventional lift-off, a "dry" lift-off technique of the invention was carried out by simply peeling the mask from the surface and allowing the gold to remain adhered to the silicon surface at regions in register with channels 32. Fig. 9 is an SEM image of resulting 50 micron circles of gold patterned on a silicon substrate according to this example. Excellent edge resolution of the gold features was observed.

25 Example 3: A "Dry" Lift-Off Method: (B) Etching Through an Elastomeric Mask Followed by Removal of the Mask

As in Example 2, an agent was delivered through a mask: in this example the agent was an etchant. A PDMS mask containing circular channels of 3 microns in diameter, separated by 7 microns, was brought into conformal, sealing contact with a silicon substrate. The masked surface was then exposed to Reactive Ion Etching (RIE), i.e., SF<sub>6</sub> gas in a plasma discharge for 8 min. The mask was then removed from the surface to reveal "wells" etched into the silicon that were in register with the channels in the PDMS mask. Patterning by RIE



usually requires photolithography to create a mask followed by a wet lift-off: these two steps are bypassed by using an elastomeric mask. Fig. 10 is an SEM image of the 3 micron diameter wells in silicon. Such structures could be used as nanovials for chemical analysis of very small volumes of samples.

5 Example 4: Fabrication of Single-Color and Multicolor Electroluminescent Pixels

A PDMS mask containing circular channels of 500 microns in diameter, separated by 500 microns, was brought into conformal, sealing contact with an indium tin oxide (ITO) layer patterned on a glass substrate. In alternate procedures, a PDMS mask containing either an array of circular holes (3  $\mu\text{m}$ , spaced by 3  $\mu\text{m}$ ) or an alphanumeric pattern (smallest  
10 dimension  $\sim 100 \mu\text{m}$ ) sealed conformally against a silicon substrate when brought into contact with it. An electroluminescent material, tris (8-hydroxyquinoline)-aluminum ( $\text{Alq}_3$ , 50 nm) was deposited by thermal evaporation (rate of deposition  $\sim 0.5 \text{ nm/s}$ ; base pressure  $\sim 5 \times 10^{-6}$  Torr) onto the mask and substrate. Peeling the elastomeric mask from the substrate left features of  $\text{Alq}_3$  on the surface patterned as circles or alphanumeric characters. An aluminum  
15 cathode then was evaporated on top of the arrangement and an electrical potential was applied between the aluminum cathode and the ITO anode. Fig. 11 shows an image of the electroluminescence from 500 micron diameter pixels. Figs. 12 and 13 show photoluminescence images of  $\text{Alq}_3$  pixels with diameters of 50 and 3 microns, respectively, patterned on a silicon substrate.

20 Multicolor pixels based on organic electroluminescent molecules can be created easily using two PDMS masks. A PDMS mask containing circular channels of 100 microns in diameter, separated by 100 microns, was brought into conformal, sealing contact with a substrate. A second mask containing rectangular channels 1 mm long and 150 microns wide, spaced by 300 microns, was sealed against the first mask so that the openings in the upper  
25 mask was aligned with every third line of channels in the lower mask. A mixture of 1,1,4,4-tetraphenyl-1,3-butadiene (TPB), which gives rise to blue electroluminescence, and Nile Red dye was thermally evaporated through the masks to pattern the first line of pixels. The upper mask was then re-placed by being removed and realigned with the line of pixels adjacent to those exposed previously: Nile Red dye was then evaporated through the masks to  
30 pattern a second line of pixels. The upper mask was then removed and realigned with the remaining line of unpatterned pixels:  $\text{Alq}_3$  was then evaporated through the masks. Lines of pixels of molecules that display red, green, and blue electroluminescence were revealed when

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both the upper and lower masks were removed. A photoluminescence image of red, green, and blue pixels with 100 micron diameters spaced by 100 microns created using two PDMS masks was observed. The use of two PDMS masks in this way saves several steps of photolithography and encapsulation that are usually needed to pattern multicolor displays.

5 Example 5: Application of Agent From the Liquid Phase: Electroplating through an Elastomeric Mask

Unlike conventional shadow masks, the conformal seal of the PDMS masks with the substrate to be patterned makes it possible to deposit materials from the liquid phase, for example, by electroplating. A PDMS mask containing circular channels of 50 microns in  
10 diameter, separated by 50 microns, was brought into conformal, sealing contact with a gold substrate, to create "wells" whose sides were defined by the channels in the mask and whose

bottom was defined by the gold surface. The substrate was cleaned for 30 s using a plasma cleaner (Harrick, PDC-23C) to render the surface of the mask hydrophilic so that the plating solution would wet it. A drop of triethylene glycol was then  
15 put on top of the mask to fill the wells; air trapped in the wells was removed by vacuum. The substrate and mask was then placed in a silver electroplating solution: electroplating silver from a plating bath (Technic Silver E2, Technic, Providence, RI: current density  $\sim 20$  mA/cm<sup>2</sup>) onto the regions of the gold surface in register with the channels in the PDMS produced metallic microstructures on the conductive substrate. After removal of the mask,  
20 these structures remained on the surface. Fig. 14 is an optical image of the 50 micron diameter circles of silver electroplated onto gold.

Example 6: Application of Agent From the Liquid Phase followed by Solidification: Patterning Glassy Features using Sol-Gel Chemistry and Elastomeric Masks

A PDMS mask containing circular channels of 50 microns in diameter, separated by  
25 50 microns, was brought into conformal, sealing contact with a silicon substrate. 6.5 g tetramethylorthosilicate (TMOS) and 1.5 g 0.1 M oxalic acid were mixed for 1 min and left to stand for 1 h: a drop of this mixture was placed on top of the PDMS mask and a vacuum was applied to remove air from the wells (described in Example 5) filled with liquid. The silicon substrate and mask were tilted to drain the liquid from the surface, and then left in a sealed  
30 container along with a drop of ammonium hydroxide for 18 h. The acidified TMOS solution gels by hydrolysis and polycondensation under basic conditions to yield a glassy material: when the PDMS mask was removed from the silicon substrate, glassy structures in register

with the channels in the mask were revealed. Fig. 15 is an optical image of the circles of solid glass on silicon created using this method.

Example 7: Application of a Biological Agent From the Liquid Phase: Patterning Proteins Through an Elastomeric Mask

5 A PDMS mask containing circular channels of 3 microns in diameter, separated by 7 microns, was brought into conformal, sealing contact with a gold surface coated with a monolayer of hexadecanethiol. A buffer solution (100 mM Tris, 20 mM boric acid) containing 2 mg/ml of a protein, bovine carbonic anhydrase, that had been fluorescently labeled with fluorescein isothiocyanate was prepared. A drop of the solution of protein was  
10 placed on the PDMS mask to fill the wells defined by the channels in the mask and the hydrophobic gold surface; trapped air was removed by vacuum. Only the areas of gold in register with the channels in the mask were exposed to the protein solution: the conformal seal ensured that liquid did not seep onto the other region of gold. After 2 h, the substrate and mask were washed with buffer solution and dried. The PDMS mask was then removed.  
15 Fluorescence images (Fig. 16) reveal that protein had adsorbed to the hydrophobic gold surfaces only in register with the channels in the mask.

Example 8: Formation of Inter-Connected Pattern by Re-Placement of Masking System

An adhesion promoter (Ti, 5nm), followed by gold (50 nm) was evaporated through a mask containing an array of staggered crosses (Fig. 17). Performed dry lift-off once, and then  
20 translated the mask, deposited material again, and performed a second lift-off step to produce a square grid (Fig. 18).

Example 9: Application of Hydrogel Pattern Through a Mask

We sealed a PDMS mask (50  $\mu$ m circles, spaced by 50  $\mu$ m) on a glass side that had been cleaned in piranha solution (concentrated  $\text{H}_2\text{SO}_4$ /30%  $\text{H}_2\text{O}_2$  (3:1): *Caution: piranha solution can react violently with organic materials and should be handled with care*) and then  
25 oxidized for 60 s in a plasma cleaner: this step rendered the mask and substrate hydrophilic and easily wetted by the solution. A drop of a solution of gelatin (KNOX, Nabisco, Inc., East Hanover, NJ) was then placed at 60°C on the sample so that the mask was completely covered with solution. After the sample was degassed under vacuum (10-20 s) to remove air trapped  
30 in the wells formed by the mask in contact with the substrate, we placed the sample back in the oven at 60° C and allowed the solution to dewet from the substrate, leaving solution in the wells. The sample was then left at room temperature to allow the solution to set and then

removed the mask, leaving an array of patterned gelatin on the substrate (circles of approximately 50 microns in diameter). Polyacrylamide gels were also patterned using a similar technique. These patterned gels have potential applications, for example, as components in diffraction-based biological sensors or to create regular arrays of discrete, small features of photographic materials.

Example 10: Application of Organometallic Compounds by Evaporation Through a Mask

Small organometallic molecules, such as tris(8-hydroxyquinoline) aluminum ( $\text{Alq}_3$ ), can be evaporated through shadow masks, or patterned photoresist, but are usually soluble in the solvents used for lift-off since they may be useful in optical displays. Thermal evaporation of  $\text{Alq}_3$  (500 Å), through an elastomeric mask, followed by dry lift-off, produced circular areas of the material. These patterns are photoluminescent and electroluminescent

when addressed electrically. Patterns were approximately 100 microns in diameter.

Example 11: Application of Conducting Polymer Precursors by Chemical Vapor Deposition (CVD) Through a Mask

We brought a mask (50  $\mu\text{m}$  holes, spaced by 50  $\mu\text{m}$ ) into contact with a substrate (Si or indium tin oxide) and placed it into a CVD system (base pressure  $\sim 0.03$  Torr). PPV was prepared from a dichloro-p-xylene starting monomer, in a method similar to CVD of parylene. The monomer ( $\alpha, \alpha'$ -dichloro-p-xylene) was heated to  $60^\circ\text{C}$  and brought to a furnace where it was pyrolyzed at  $675^\circ\text{C}$  to form a chloro-p-xylylene. This material was transported at low pressures ( $\sim 0.1$  Torr) to the deposition zone by an Ar carrier gas (flow rate  $\sim 8$  sccm) where it condensed on the substrate ( $25^\circ\text{C}$ ) and polymerized to form a PPV precursor (a chlorinated poly (1,4-xylylene)). After heating the substrate at  $150^\circ\text{C}$  for  $\sim 1$  h to partially convert the precursor, we performed dry lift-off. Further heating to  $250^\circ\text{C}$  fully converted the precursor to PPV.

Those skilled in the art would readily appreciate that all parameters listed herein are meant to be exemplary and that actual parameters will depend upon the specific application for which the methods and apparatus of the present invention are used. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described.

What is claimed is:

CLAIMS

1. A method comprising:  
shielding a first portion of a surface of an article with a masking system including a  
5 cohesive mask in conformal contact with the surface of the article; and  
allowing an agent to be applied through a channel, having a dimension of less than 1  
millimeter, within the masking system to a second portion of the surface of the article while  
preventing application of the agent to the first portion with the masking system.
- 10 2. A method as in claim 1, the shielding step involving sealing at least a portion of the  
first portion of the article surface with the flexible surface of the mask.
3. A method as in claim 2, wherein the mask is a flexible mask including a first surface,  
an opposing second surface, and a plurality of channels passing through the mask and  
15 connecting the first surface with the second surface.
4. A method as in claim 2, wherein the mask has a flexible surface, the shielding step  
involving contacting the first portion of the article surface with the flexible surface of the  
mask.
- 20 5. A method as in claim 2, involving shielding the first portion of the surface by bringing  
the flexible surface of the mask into conforming contact with the article surface.
6. A method as in claim 4, wherein the article surface is non-planar.
- 25 7. A method as in claim 2, wherein the mask is flexible in its entirety.
8. A method as in claim 2, involving shielding the first portion of the article surface with  
a mask having a polymeric surface.
- 30 9. A method as in claim 2, involving shielding the first portion of the article surface by  
bringing an elastomeric surface of the mask into conformal contact with at least a portion of

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the first portion.

10. A method as in claim 9, wherein the first portion of the article surface is non-planar.

5 11. A method as in claim 9, further comprising removing a mask from at least a portion of the first portion of surface of the article while allowing the agent or a product of the agent to remain at the second portion of the surface of the article.

12. A method as in claim 11, further comprising re-placing a mask in relation to the  
10 surface of the article, and applying an agent to at least a portion of the first portion of the surface of the article.

13. A method as in claim 12, the re-placing step involving re-orienting a mask in relation to the surface of the article.

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14. A method as in claim 12, the re-placing step involving removing the mask from the surface of the article and applying an agent to at least a portion of the first portion of the surface without shielding the surface with the mask.

20 15. A method as in claim 2, further comprising re-placing a mask in relation to the surface of the article, and applying an agent to at least a portion of the first portion of the surface of the article.

16. A method as in claim 2, wherein a mask of the masking system has a thickness,  
25 defining channel length, of no more than about 500 microns.

17. A method as in claim 2, wherein a mask of the masking system includes a plurality of channels within it and the second, unshielded portion of the surface of the article includes a plurality of portions in register with channels of the mask, and the allowing step involves  
30 applying the agent through the plurality of channels to the portions of the surface defining the second, unshielded portion.

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18. A method as in claim 17, wherein the mask includes at least 100 channels, and at least 50 percent of the channels have a cross-sectional dimension of less than about 200 microns.

19. A method as in claim 18, wherein at least about 98 percent of the channels have a  
5 cross-sectional dimension of less than about 200 microns.

20. A method as in claim 19, wherein at least about 98 percent of the channels have a maximum cross-sectional dimension of less than about 200 microns.

10 21. A method as in claim 20, wherein the mask is a flexible polymeric article.

22. A method as in claim 21, wherein the mask is elastomeric.

23. A method as in claim 18, wherein the mask includes at least about 500, essentially  
15 straight, circular cross-sectional channels, each channel of cross-section of less than about 200 microns, and each channel spaced from an adjacent channel by no more than about 400 microns.

24. A method as in claim 23, wherein the plurality of channels are arranged in a grid  
20 pattern.

25. A method as in claim 23, wherein the channels have a length-to-diameter ratio of no more than about 5 to 1.

25 26. A method as in claim 23, wherein the channels have a length-to-diameter ratio of no more than about 2 to 1.

27. A method as in claim 23, the mask including at least about 1,000 channels, each of cross-section of less than about 100 microns and each channel spaced from an adjacent  
30 channel by no more than about 200 microns.

28. A method as in claim 27, wherein each of the channels has a cross-sectional dimension

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of no more than about 50 microns and each channel is spaced from an adjacent channel by no more than about 100 microns.

29. A method as in claim 27, wherein each of the channels has a cross-sectional dimension  
5 of no more than about 25 microns and each channel is spaced from an adjacent channel by no more than about 50 microns.

30. A method as in claim 27, wherein each channel has a cross-sectional dimension of no more than about 10 microns.

10

31. A method as in claim 27, wherein each channel has a cross-sectional dimension of no more than about 5 microns.

32. A method as in claim 27, wherein each channel has a cross-sectional dimension of no  
15 more than about 3 microns.

33. A method as in claim 27, wherein each channel has a cross-sectional dimension of no more than about 1.5 microns.

20 34. A method as in claim 2, wherein the agent is an organic electroluminescent material or a precursor thereof.

35. A method as in claim 34, further comprising allowing an organic electroluminescent material to form from the agent at the second portion of the surface, and establishing electrical  
25 communication between the organic electroluminescent material and an electrical circuit.

36. A method as in claim 2, wherein the agent is a liquid or is carried in a liquid.

37. A method as in claim 2, wherein the agent is the product of chemical vapor deposition.  
30

38. A method as in claim 2, wherein the agent is a product of deposition from a gas phase.



39. A method as in claim 38, wherein the agent is a product of e-beam deposition, evaporation, or sputtering.

40. A method as in claim 2, wherein the agent is a product of electrochemical deposition.

41. A method as in claim 2, wherein the agent is a product of electroless deposition.

42. A method as in claim 2, wherein the agent is applied from a fluid precursor through the channel.

43. A method as in claim 42, wherein the fluid precursor comprises a solution or suspension of an inorganic compound and the allowing step comprises allowing the inorganic compound to harden at the second portion of the article surface.

44. A method as in claim 42, wherein the fluid precursor comprises a suspension of particles in a fluid carrier and the allowing step comprises allowing the fluid carrier to dissipate thereby depositing the particles at the first region of the substrate surface.

45. A method as in claim 42, wherein the fluid precursor comprises a chemically active agent in a fluid carrier, and the allowing step comprises allowing the fluid carrier to dissipate thereby depositing the chemically active agent at the first region of the substrate surface.

46. A method as in claim 45, wherein the chemically active agent is a prepolymeric species and the allowing step comprises forming a polymeric article from the prepolymeric species.

47. A method as in claim 45, wherein the chemically active agent is an agent capable of promoting deposition of a material.

48. A method as in claim 42, wherein the agent is an etchant and the method further involves allowing the second portion of the surface of the article to be etched.

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49. A method as in claim 2, wherein the agent is an etchant and the method further involves allowing the second portion of the surface of the article to be etched.

50. A method as in claim 2, further comprising removing the flexible surface of a mask of  
5 the masking system from the first portion of the article surface while leaving the agent adhered to the second portion of the article surface.

51. A method comprising:  
shielding a first portion, having a dimension of less than 1 millimeter, of a surface of  
10 an article with a mask while leaving a second portion of the surface of the article remaining unshielded by the mask, by positioning the mask in conformal contact with the surface

applying an agent to the second portion of the surface of the article.

15 52. A method comprising:  
shielding a first portion of a non-planar surface of an article with a mask by bringing a surface of the mask into conformal contact with the non-planar surface of the article; and  
allowing an agent to pass through a channel within the mask having a dimension of less than 1 millimeter and to be applied to a second portion of the surface of the article while  
20 preventing application of the agent to the first portion with the mask.

53. A method comprising:  
shielding a first portion of a surface of an article with a masking system by bringing a surface of the masking system into conformal contact with a surface of the article;  
25 allowing an agent to be applied to a second, unshielded portion of the surface of the article while preventing application of the agent to the first portion of the surface of the article with the masking system;  
re-placing the masking system; and  
applying an agent to at least a portion of the first portion of the surface of the article.

30

54. A method as in claim 53, the shielding step involving contacting the first portion of the surface of the article with a portion of a mask, and the re-placing step involving removing the

mask from the surface and applying the agent to the first portion without shielding the surface of the article with the mask.

55. A method as in claim 53, the re-placing step involving re-orienting and re-sealing a  
5 mask of the masking system in relation to the surface of the article.

56. A method as in claim 53, wherein the masking system includes a second mask,  
positioned between a source of the agent and a first mask, the first mask positioned between  
the second mask and the surface of the article.

10

57. A method as in claim 56, wherein the first mask seals against the surface of the article  
and the second mask seals against the first mask.

58. A method as in claim 57, wherein each of the first and second masks is a flexible  
15 polymeric article.

59. A method as in claim 58, wherein each of the first and second masks is elastomeric.

60. A method as in claim 59, involving applying the agent to the second portion of the  
20 surface, re-placing the masking system by removing the second mask from the first mask  
thereby exposing at least a portion of the first portion of the surface while allowing the first  
mask to shield another portion of the first portion of the surface, and applying an agent to at  
least a portion of the first portion of the surface while shielding another portion of the first  
portion of the surface with the first mask.

25

61. A method as in claim 59, involving applying a first agent to the second portion of the  
surface, re-placing the mask by removing the second mask from the first mask thereby  
exposing at least a portion of the first portion of the surface while allowing the first mask to  
shield another portion of the first portion of the surface, and applying a second, different  
30 agent to at least a portion of the first portion of the surface while shielding another portion of  
the first portion of the surface with the first mask.

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62. A method as in claim 53, involving applying a first agent to the second portion of the surface, re-placing the mask by removing the second mask from the first mask thereby exposing at least a portion of the first portion of the surface while allowing the first mask to shield another portion of the first portion of the surface, and applying a second, different agent to at least a portion of the first portion of the surface while shielding another portion of the first portion of the surface with the first mask.

63. A method as in claim 62, wherein each of the first and second agents is a precursor of a different organic, electroluminescent material.

10

64. A method comprising:

allowing a fluid to be applied to a second portion of the surface, having a dimension of less than 1 millimeter, while preventing application of the fluid to the first portion with the mask;

allowing a material to harden from the fluid; and  
removing the mask from the surface while leaving the article adhered to the second portion of the surface.

65. A method as in claim 64, further comprising re-placing the mask and allowing a fluid to be applied to at least a portion of the first portion of the surface of the article and a material to harden from the fluid at the first portion, and removing the mask while allowing the material to adhere to the first portion of the article.

66. A method comprising:  
shielding a first portion, having a dimension of less than 1 millimeter, of a surface of an article with a mask by bringing a surface of the mask into conformal contact with the surface of the article while leaving a second portion of the surface of the article remaining unshielded by the mask;

applying an agent to the second portion of the surface; and  
without exposure of the mask to conditions of degradation, removing the mask from the surface thereby leaving the agent at the second portion of the surface and the first portion

of the surface free of the agent.

67. An elastomeric article comprising a first surface, an opposing second surface, and a plurality of channels passing through the article and connecting the first surface with the second surface, at least one of the plurality of channels having a cross-sectional dimension of less than 1 millimeter.
68. An article as in claim 67, wherein the first surface is elastomeric.
69. An article as in claim 67, wherein the article is elastomeric.
70. An article as in claim 69, comprising at least about 100 channels.
71. An article as in claim 70, wherein at least about 50% of the channels have a cross-sectional dimension of less than about 200 microns.
72. An article as in claim 71, wherein at least about 98% of the channels have a cross-sectional dimension of less than about 200 microns.
73. An article as in claim 72, wherein the mask includes at least about 500, essentially straight, circular cross-sectional channels, each channel of cross-section of less than about 200 microns, and each channel spaced from an adjacent channel by no more than about 400 microns.
74. An article as in claim 73, wherein the channels have a length-to-diameter ratio of no more than about 5 to 1.
75. An article as in claim 73, wherein the channels have a length-to-diameter ratio of no more than about 2 to 1.
76. An article as in claim 75, the mask including at least about 1,000 channels, each of cross-section of less than about 100 microns and each channel spaced from an adjacent

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channel by no more than about 200 microns.

77. An article as in claim 76, wherein each of the channels has a cross-sectional dimension of no more than about 50 microns and each channel is spaced from an adjacent channel by no more than about 100 microns.

78. An article as in claim 76, wherein each of the channels has a cross-sectional dimension of no more than about 25 microns and each channel is spaced from an adjacent channel by no more than about 50 microns.

10

79. An article as in claim 76, wherein each channel has a cross-sectional dimension of no more than about 10 microns.

80. An article as in claim 76, wherein each channel has a cross-sectional dimension of no more than about 5 microns.

81. An article as in claim 76, wherein each channel has a cross-sectional dimension of no more than about 3 microns.

82. An article as in claim 76, wherein each channel has a cross-sectional dimension of no more than about 1.5 microns.

83. A method comprising:  
immobilizing, on average, less than about  $1 \times 10^5$  molecules at each of a plurality of separate, isolated regions of a surface of an article while leaving regions of the surface of the article intervening the separate, isolated regions essentially free of the molecules.

84. A method as in claim 83, comprising applying the molecules to each of the separate, isolated regions through channels within a mask.

30

85. A method as in claim 84, comprising sealing a surface of a mask to the surface of the article creating exposed regions of the surface of the article in register with channels of the

mask, and applying the molecules to those regions of the surface of the article in register with the channels.

86. A method as in claim 85, the applying step involving applying a fluid containing the  
5 molecules to regions of the surface of the article in register with channels of the mask.

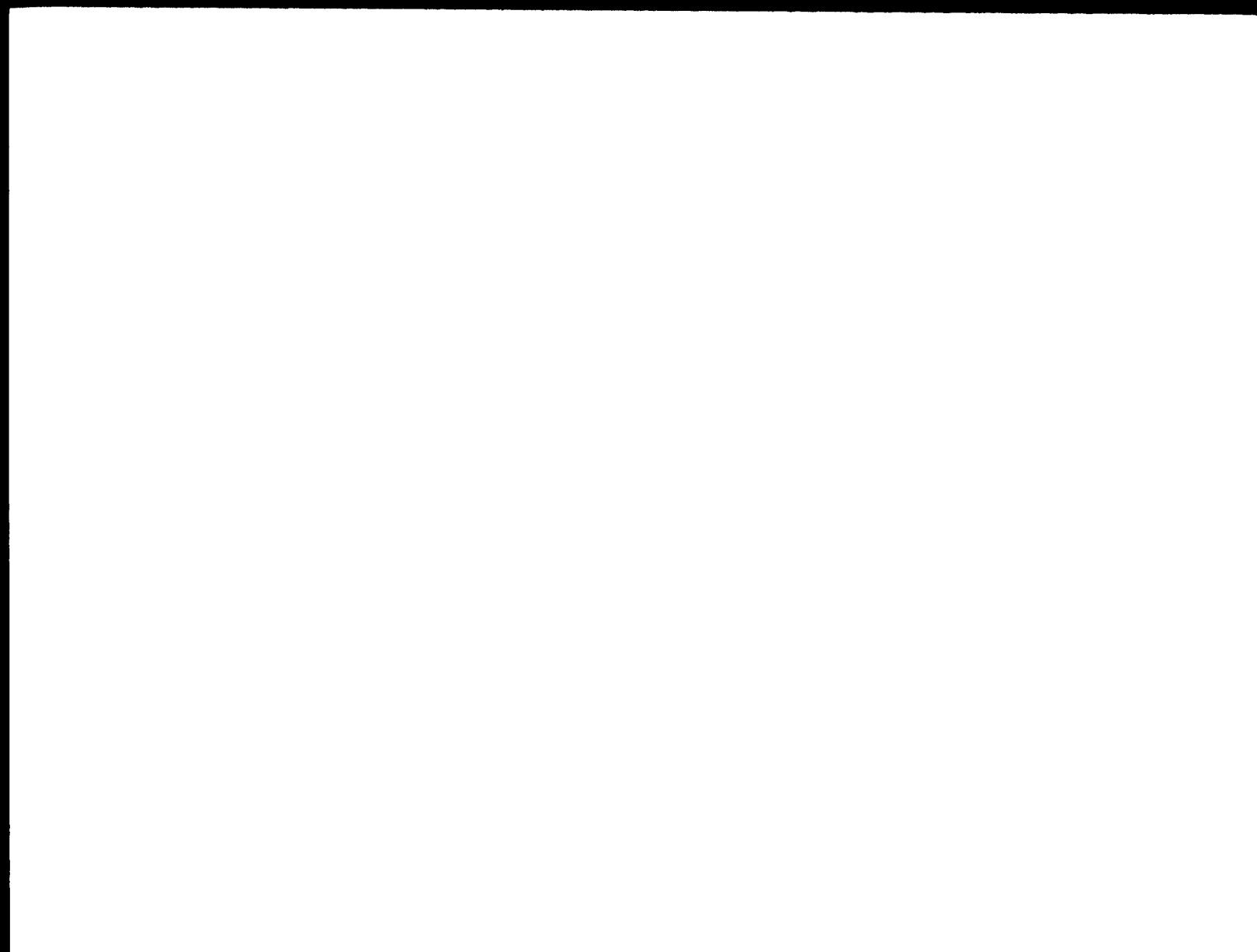
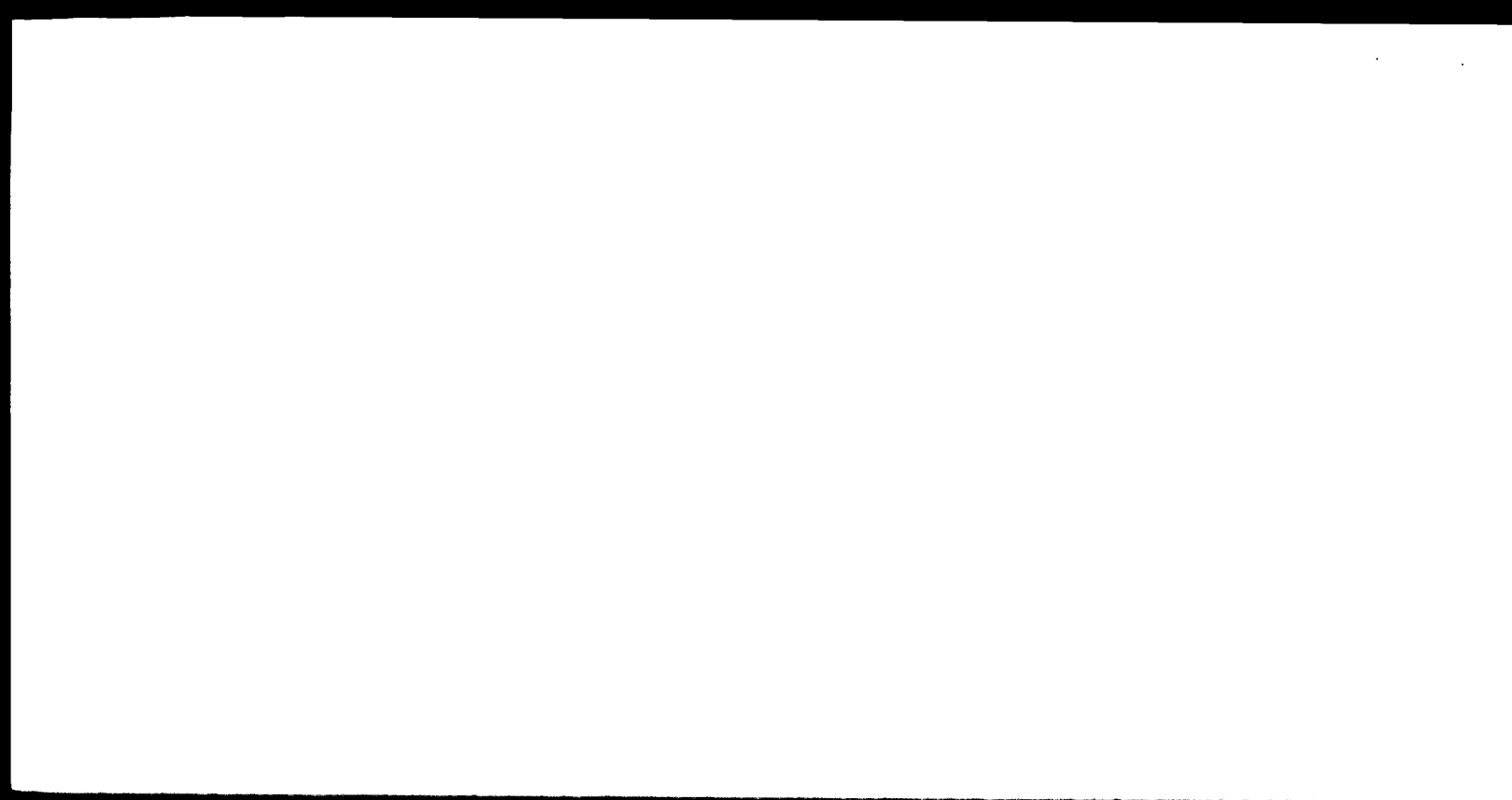
87. A method as in claim 83, comprising applying, on average, less than about  $1 \times 10^4$  molecules to each of the separate, isolated regions.

10 88. A method as in claim 83, comprising applying, on average, less than about  $1 \times 10^3$  molecules to each of the separate, isolated regions.

89. A method as in claim 83, comprising applying, on average, less than about  $1 \times 10^2$  molecules to each of the separate, isolated regions.

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90. A method as in claim 83, comprising applying, on average, less than about  $1 \times 10$  molecules to each of the separate, isolated regions.





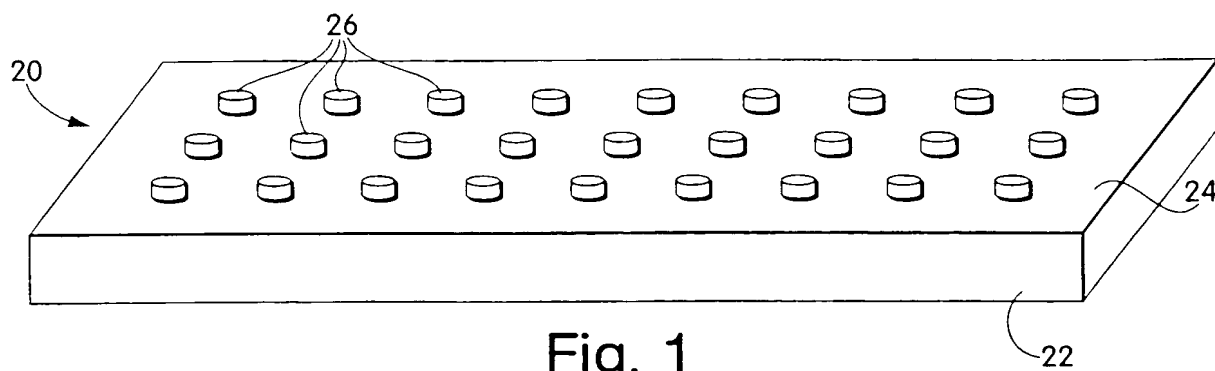


Fig. 1

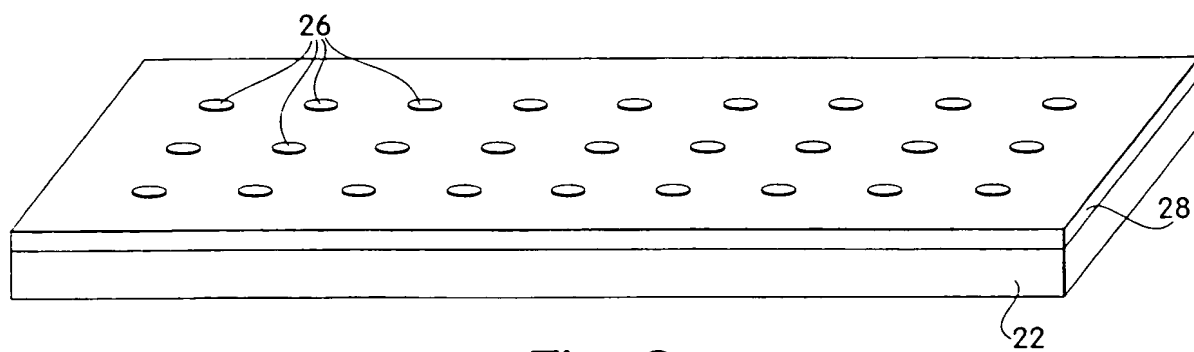


Fig. 2

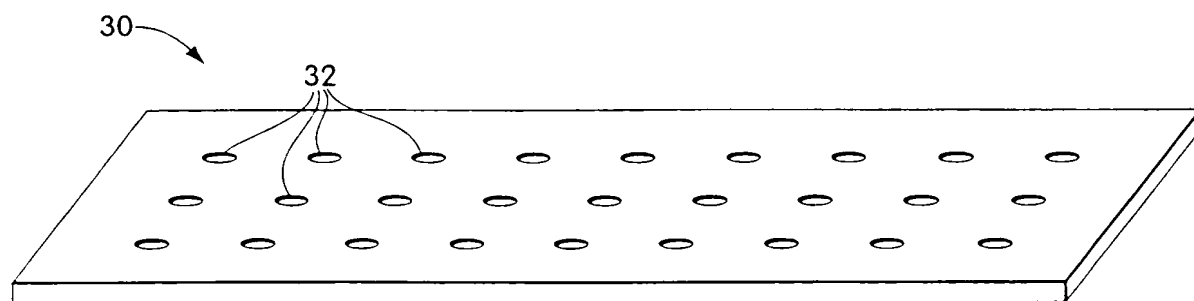
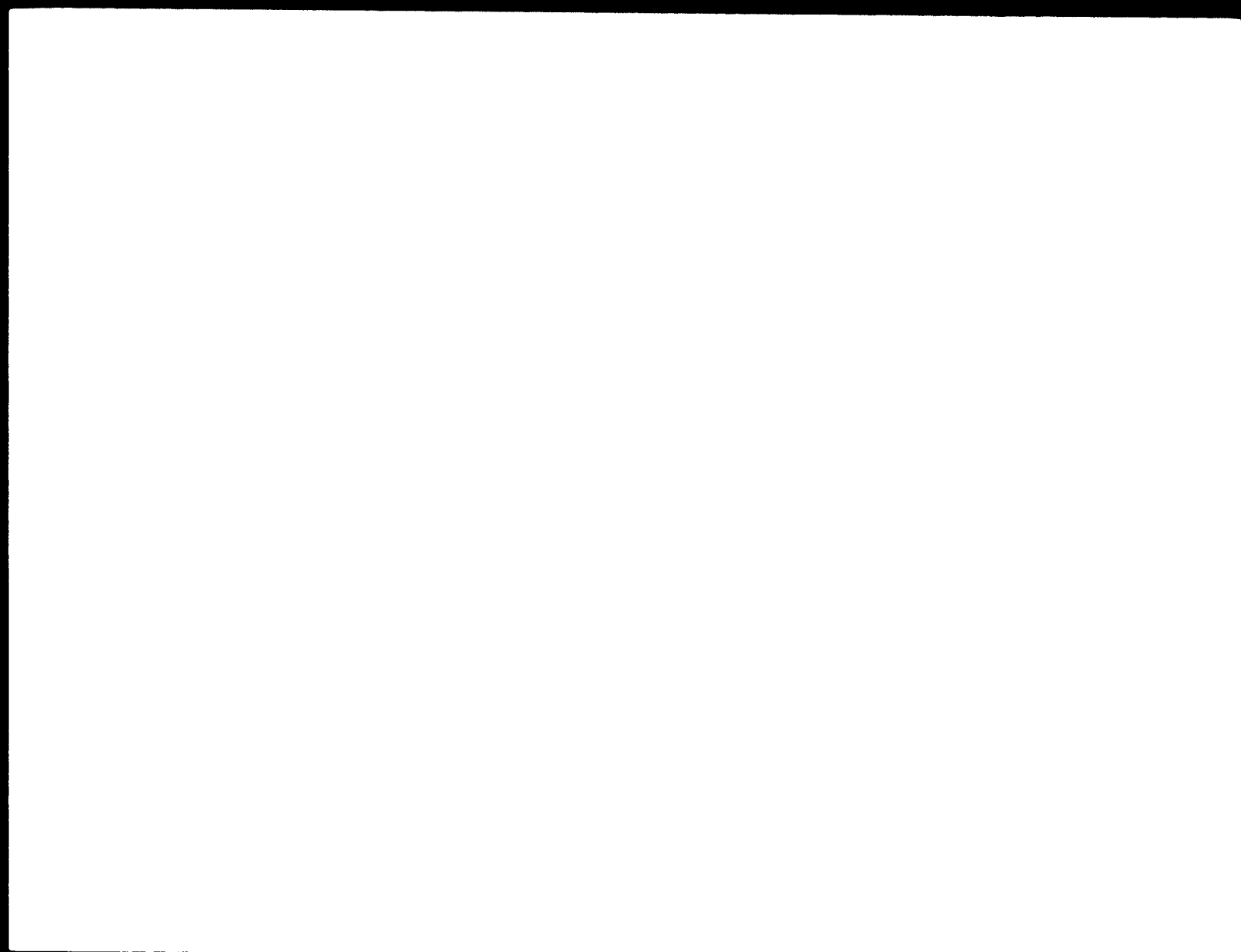
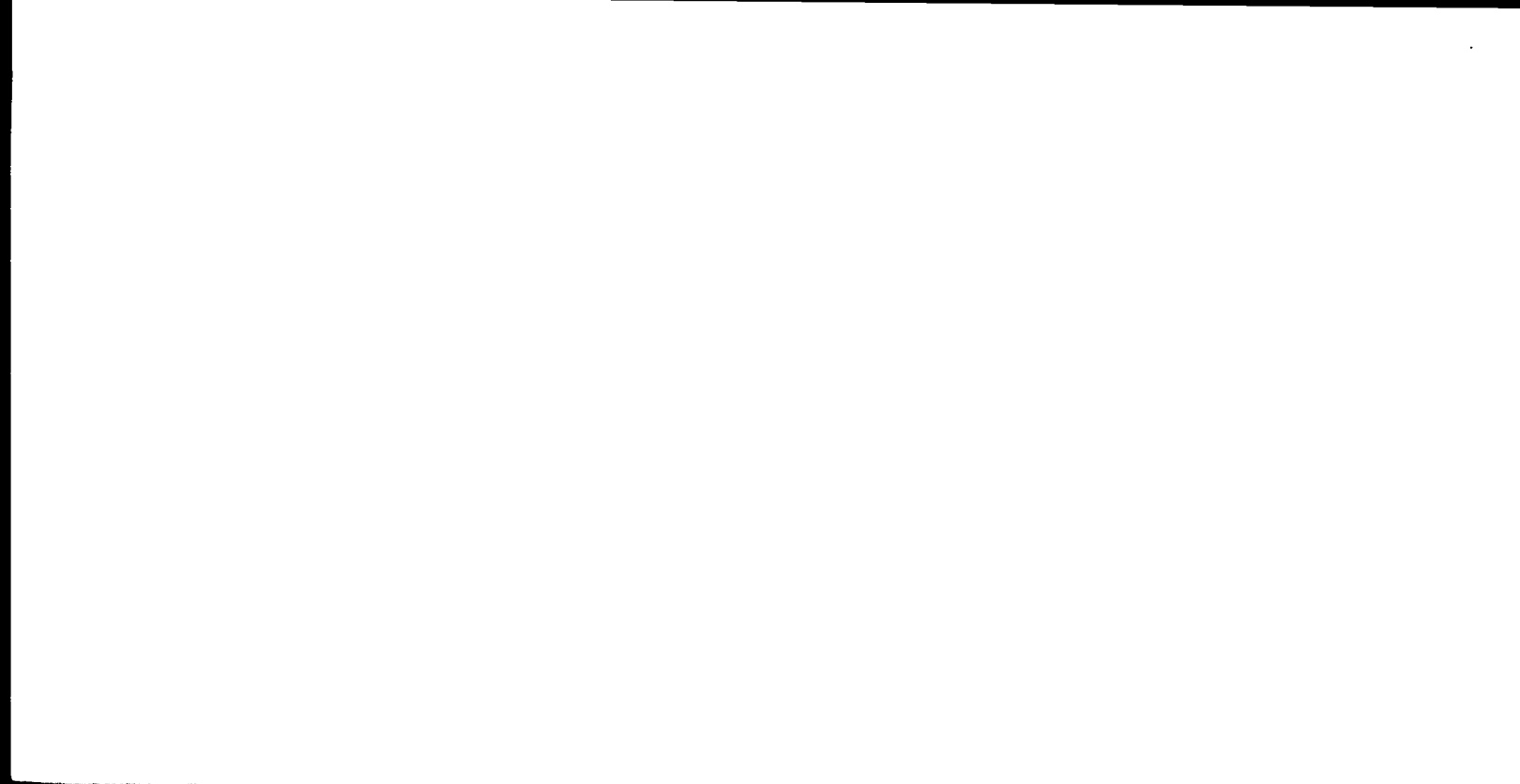


Fig. 3



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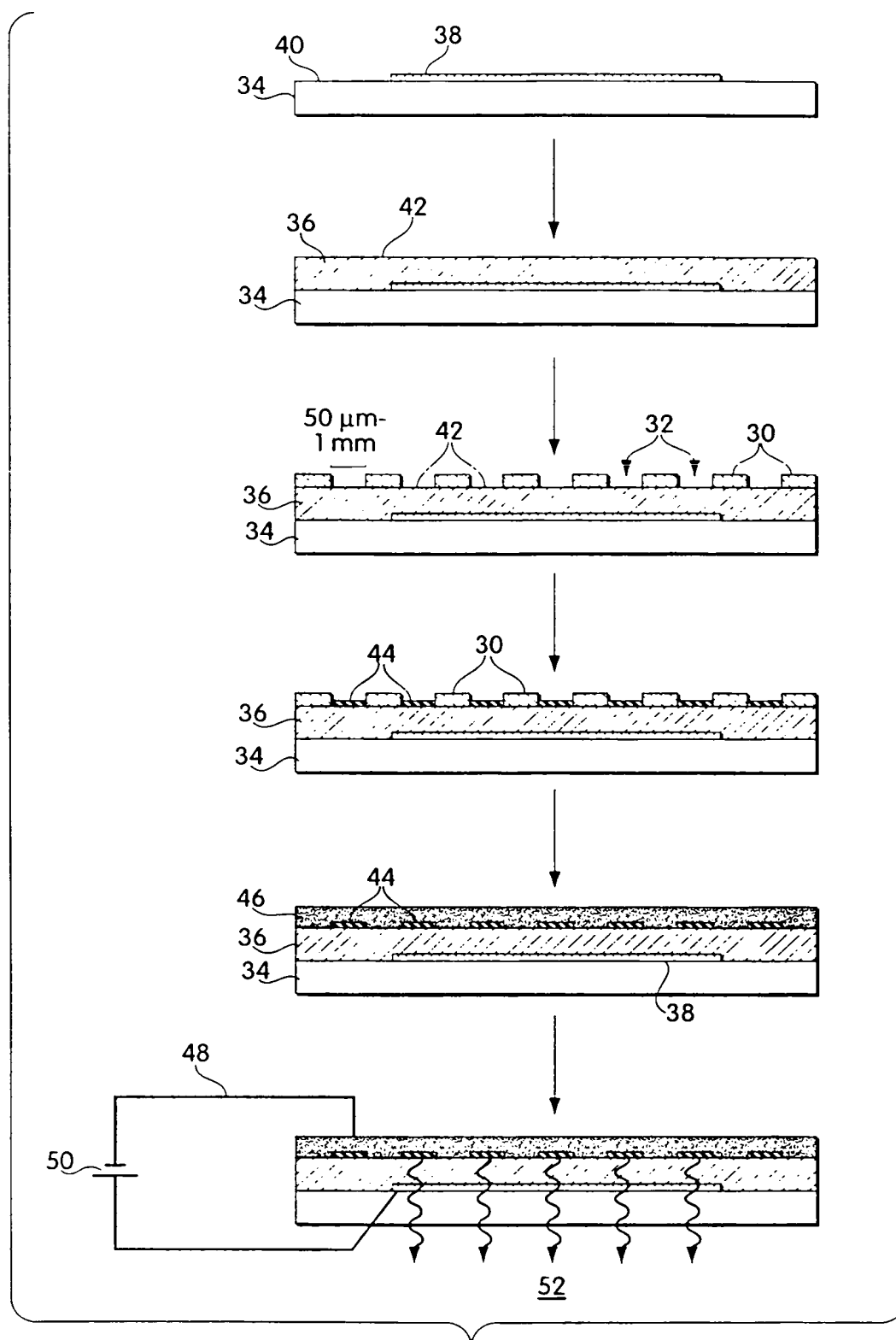
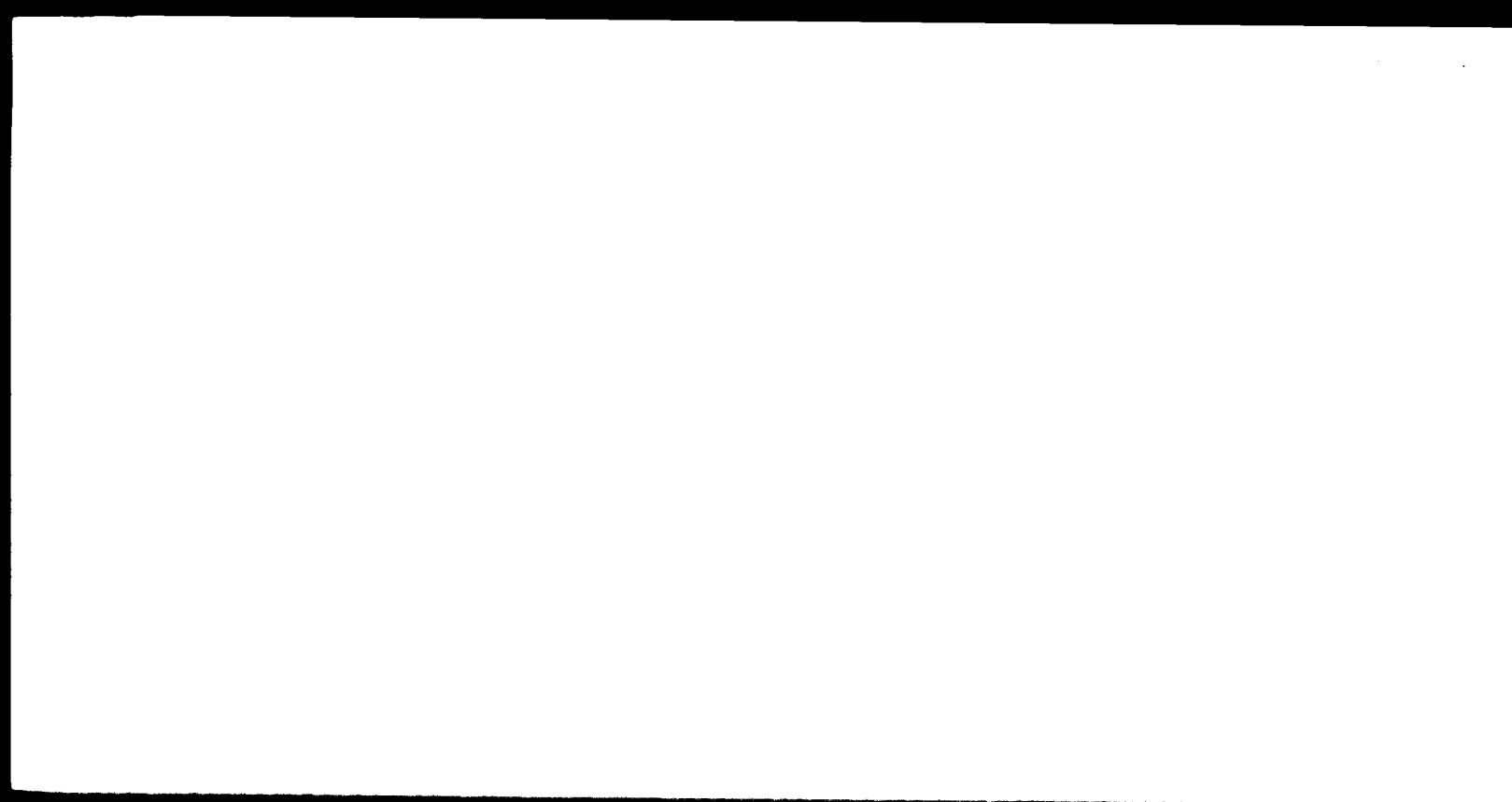


Fig. 4



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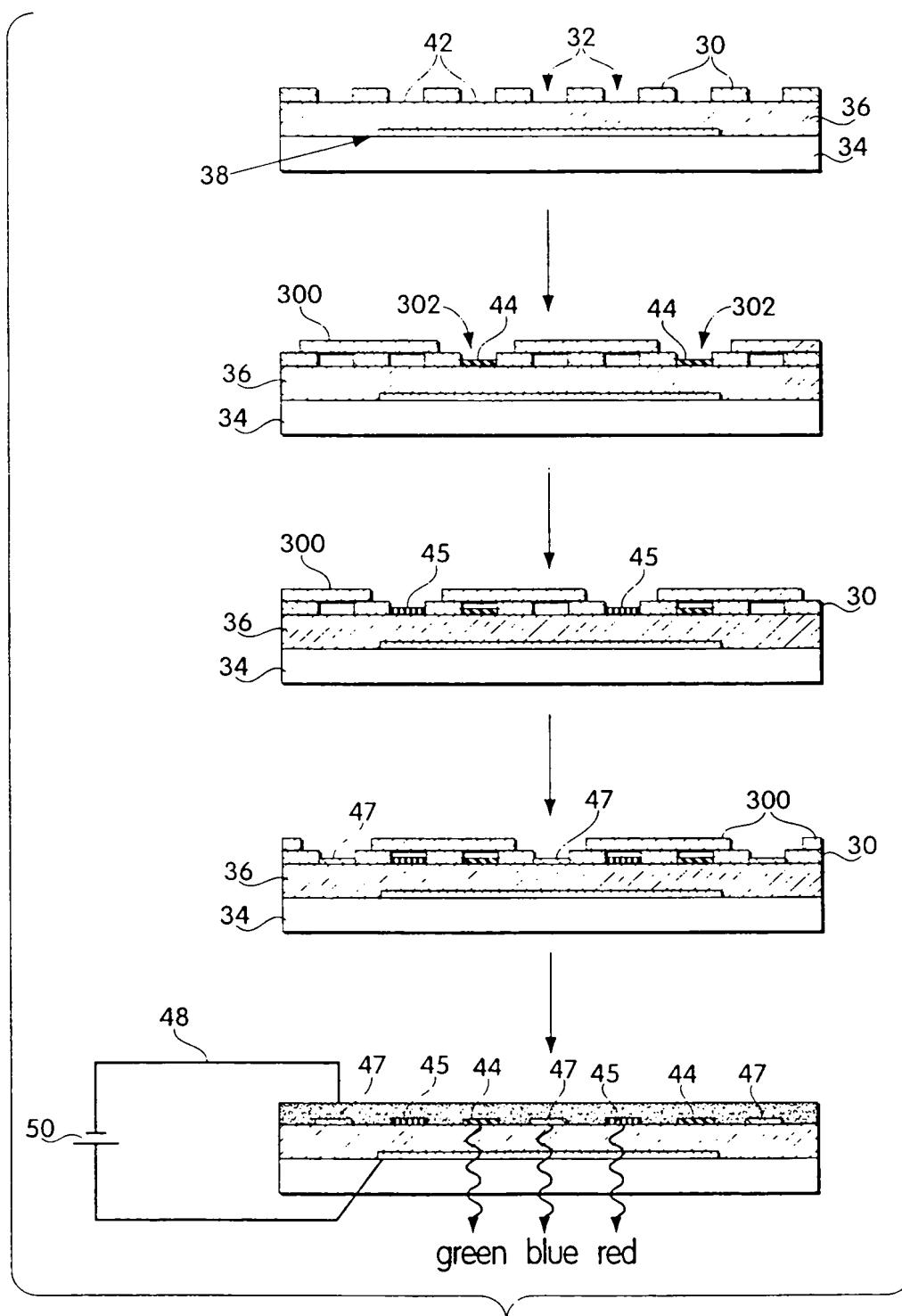
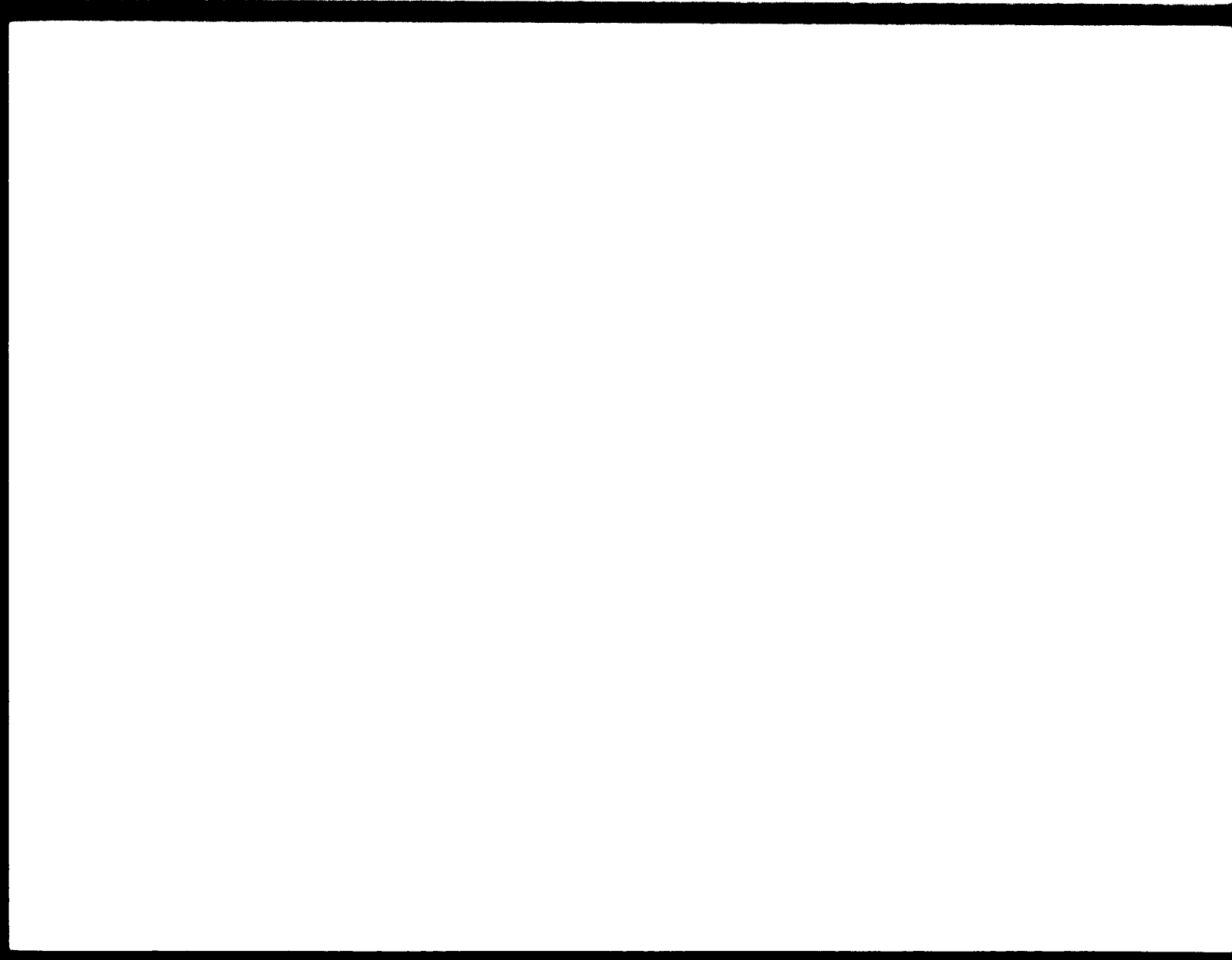


Fig. 5



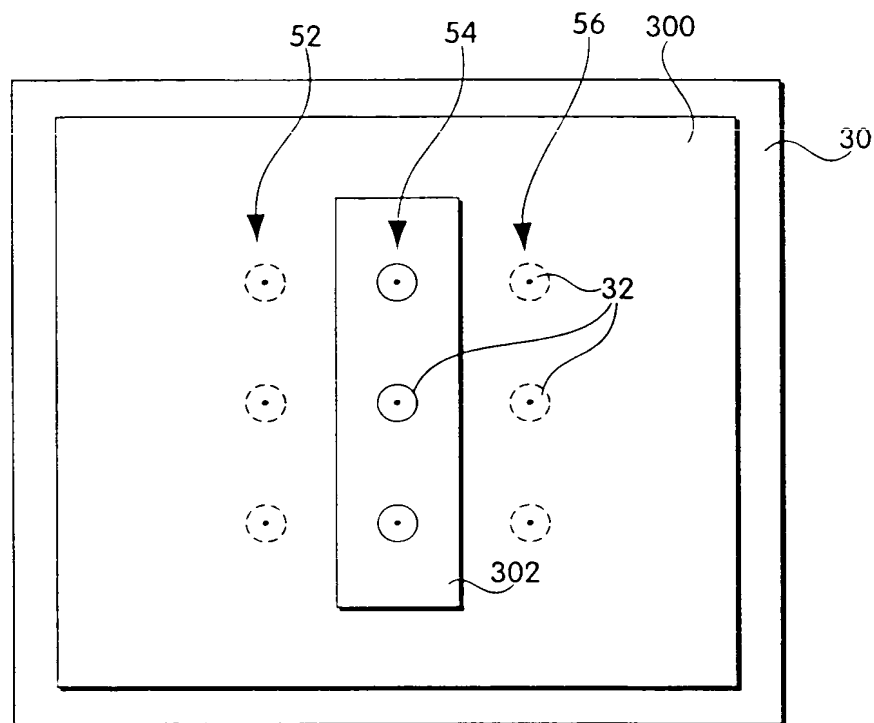
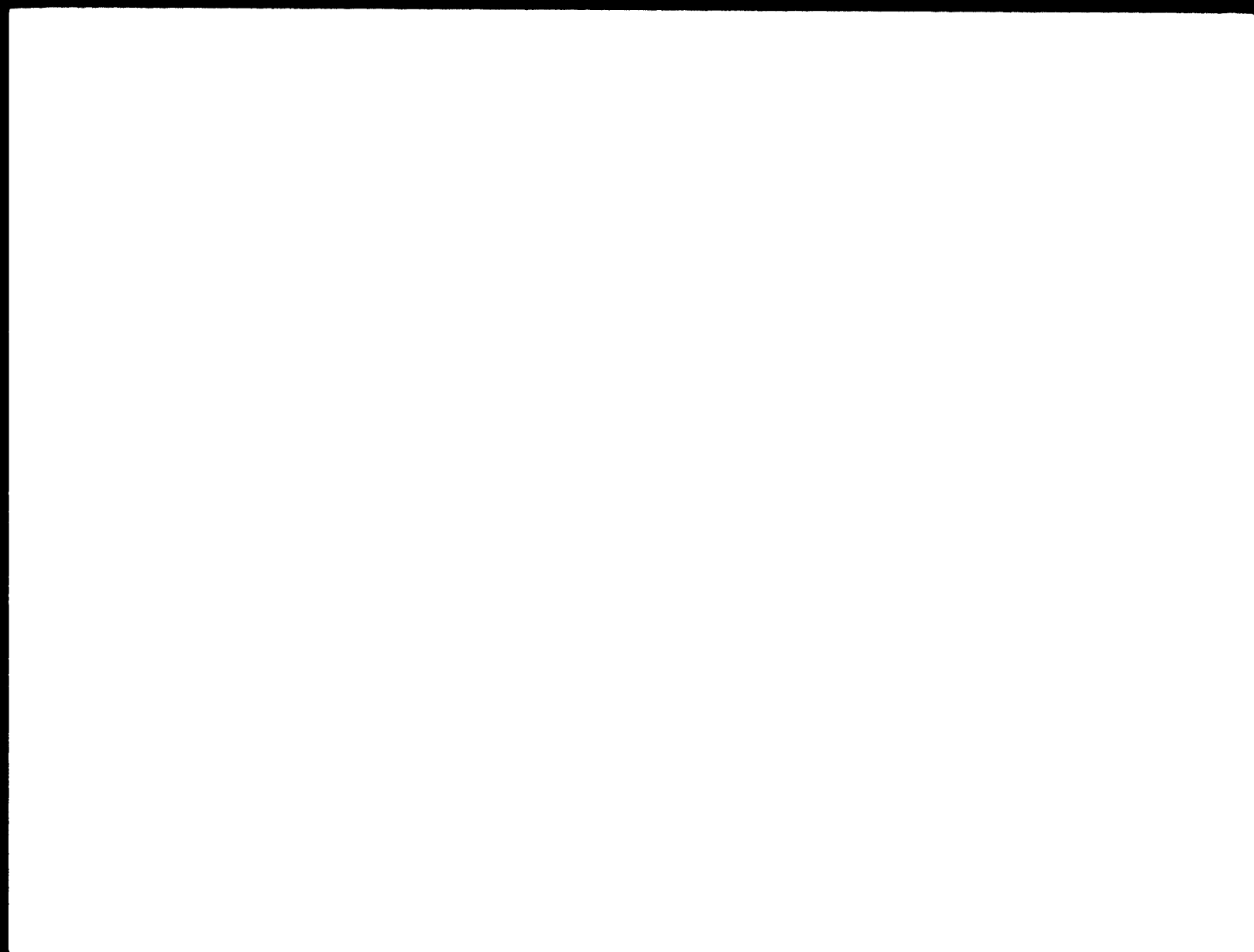
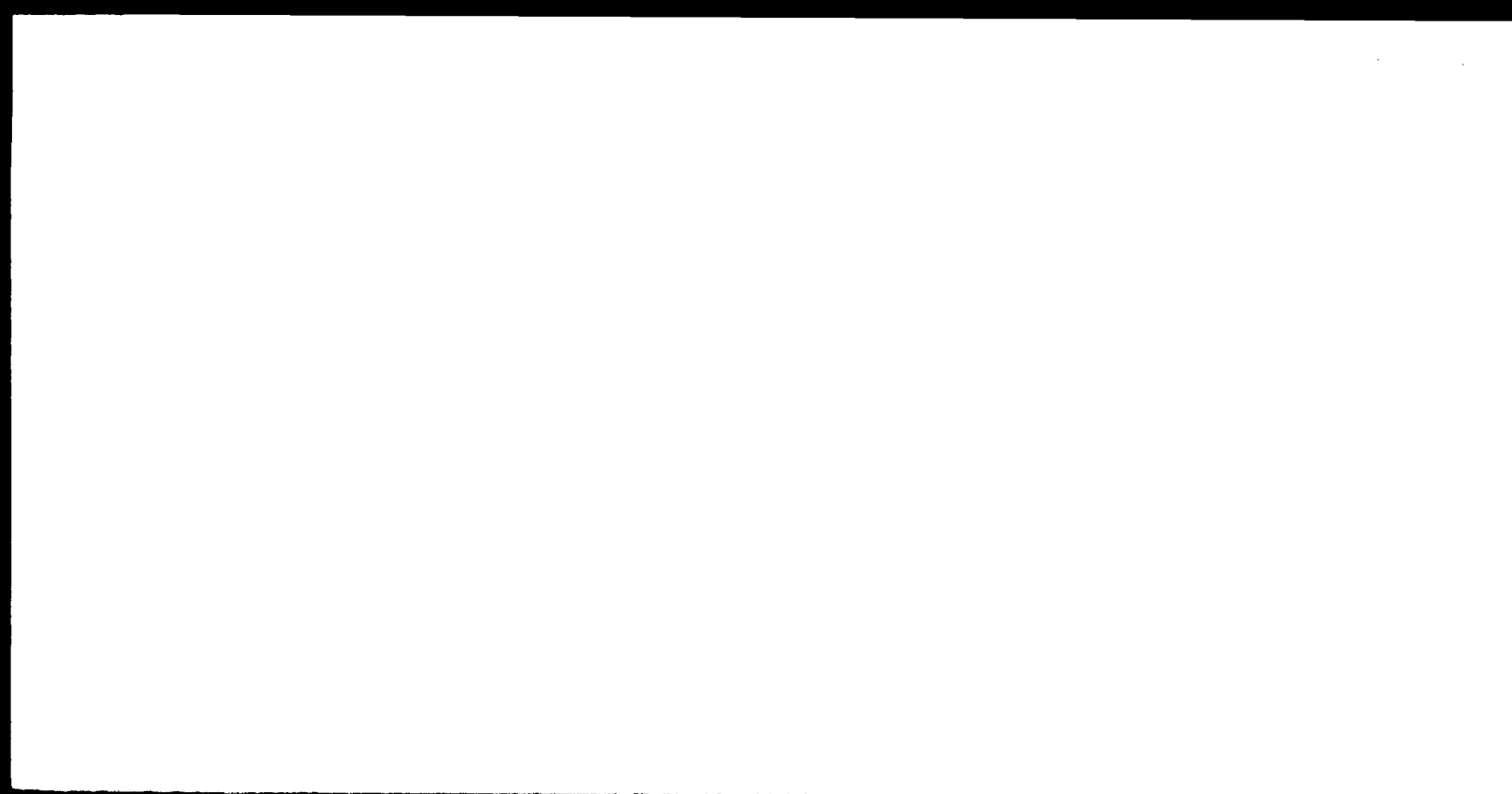


Fig. 6





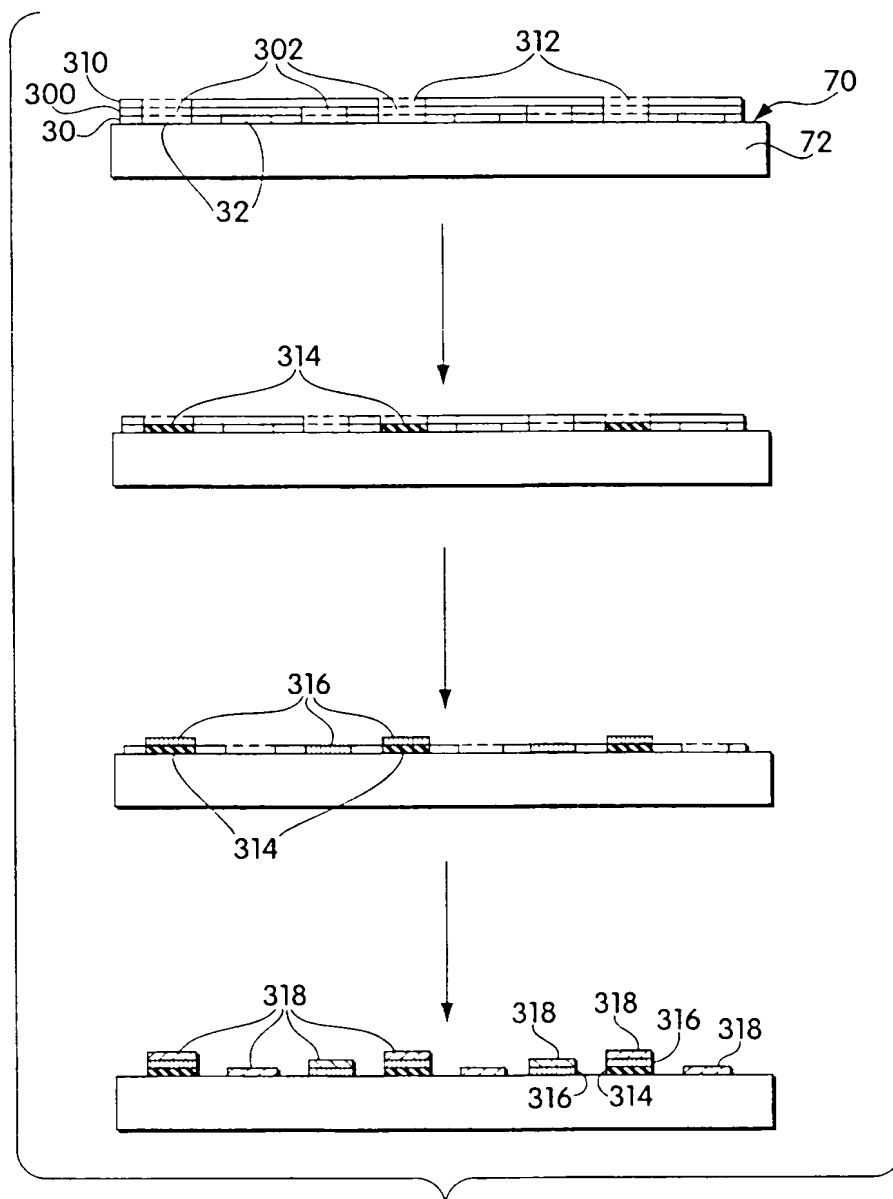


Fig. 7



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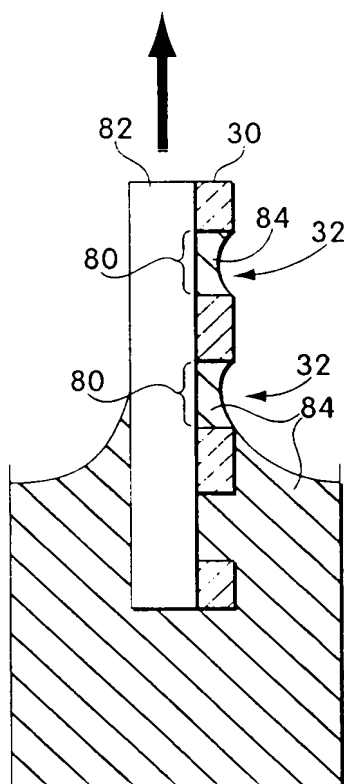


Fig. 8



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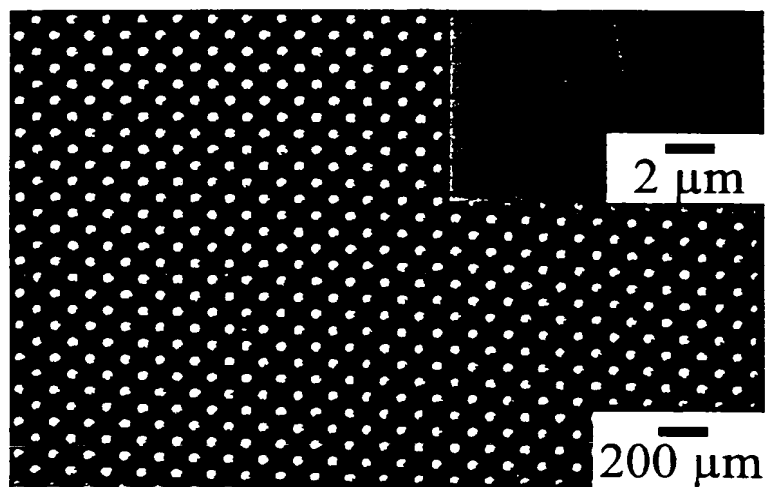


Fig. 9

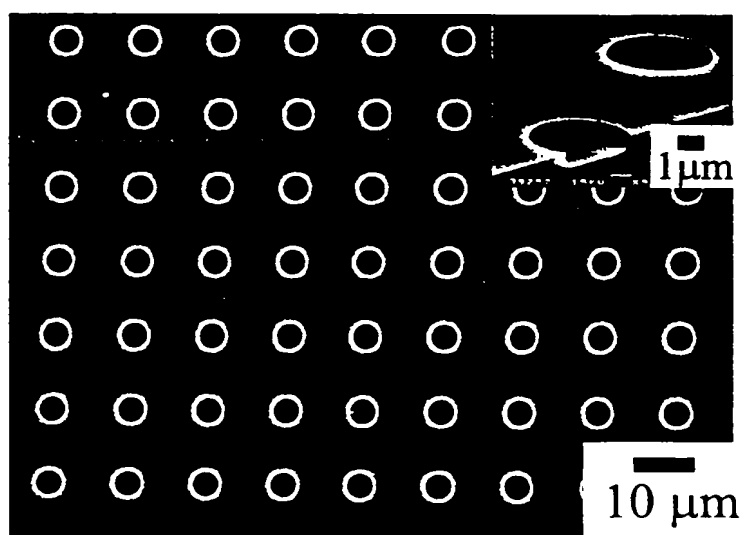
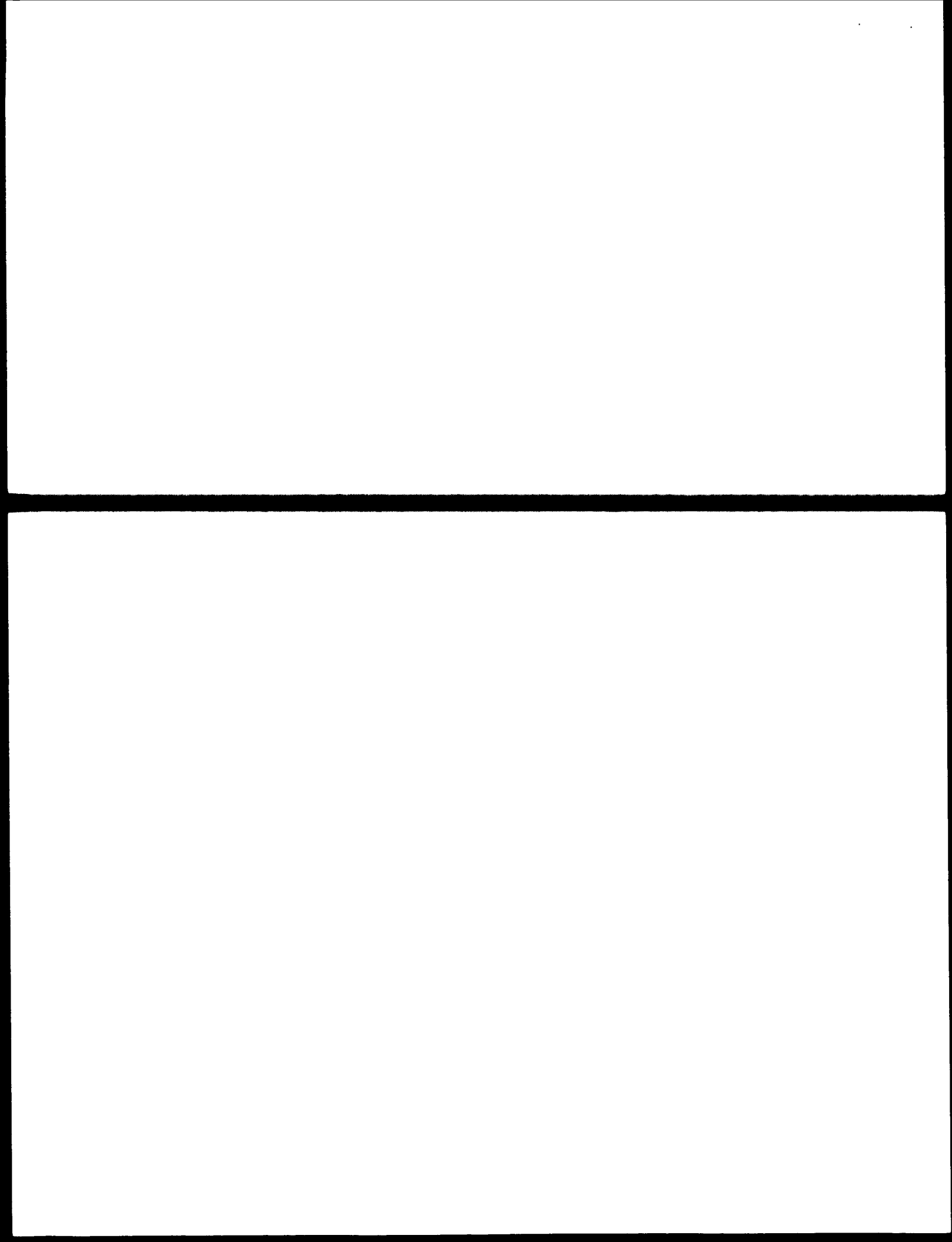


Fig. 10



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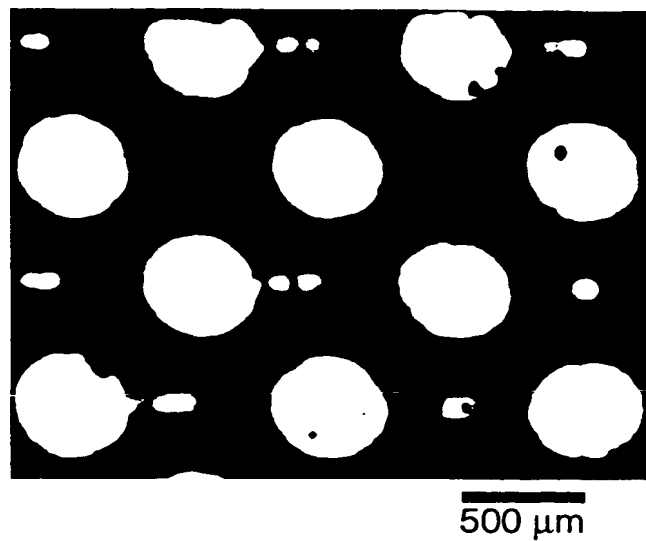


Fig. 11

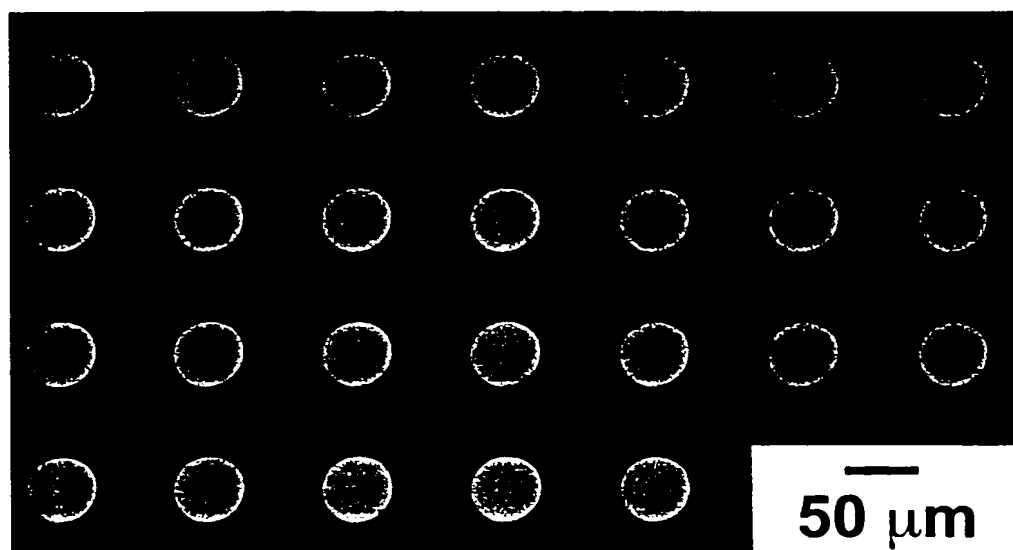


Fig. 12





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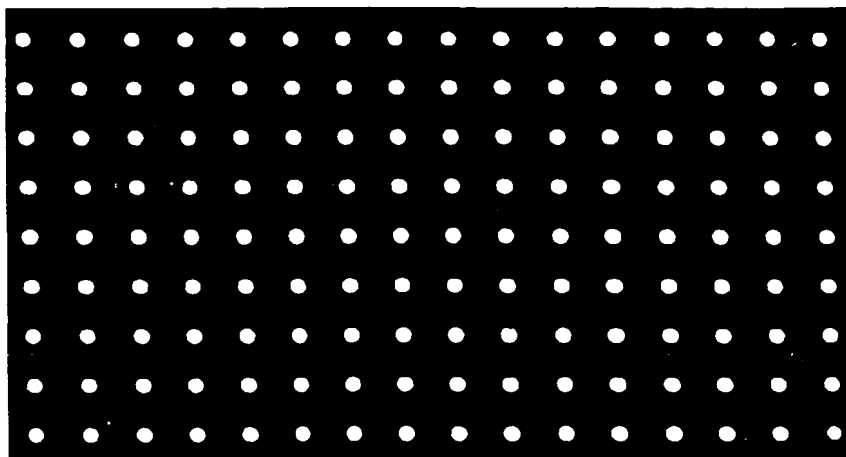


Fig. 13

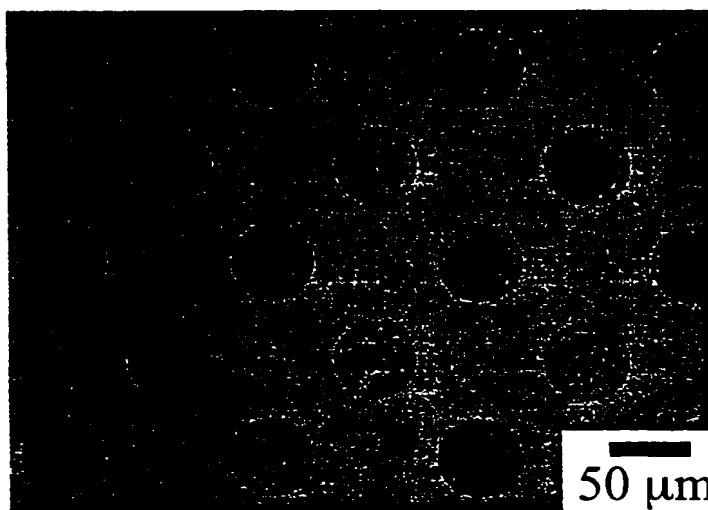
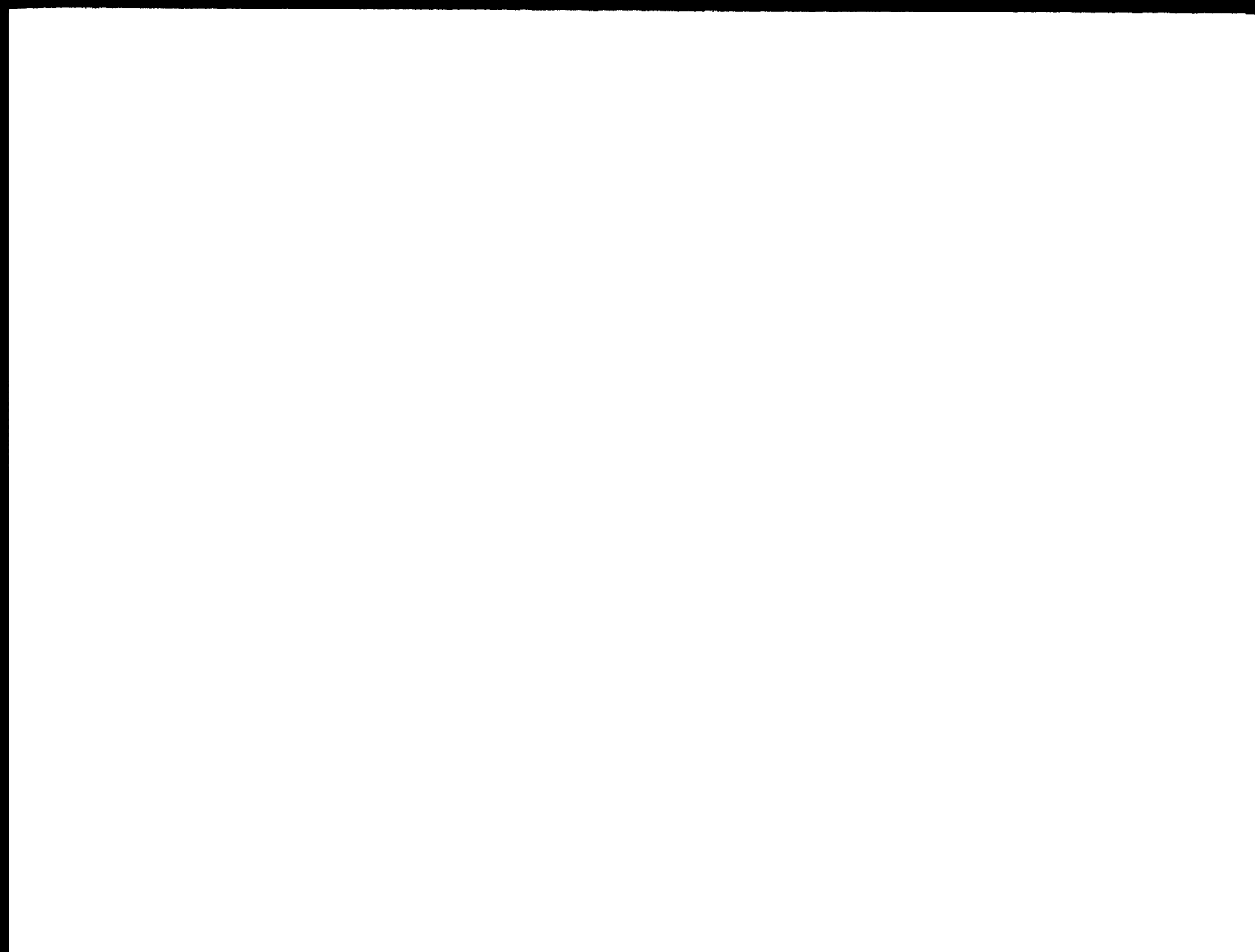


Fig. 14



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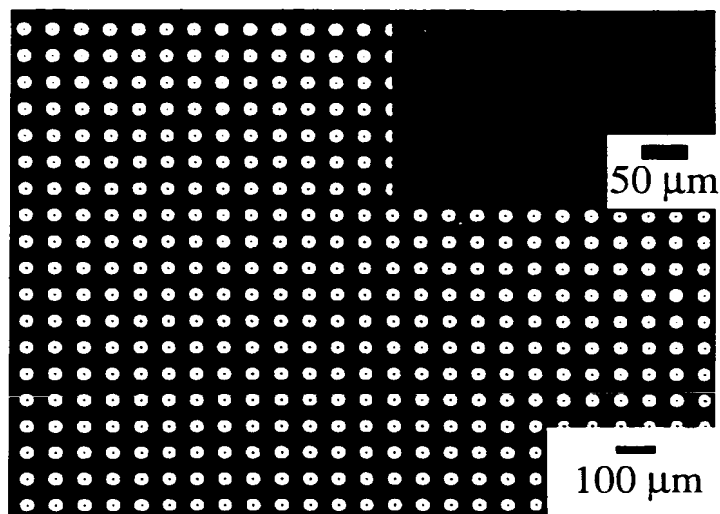


Fig. 15

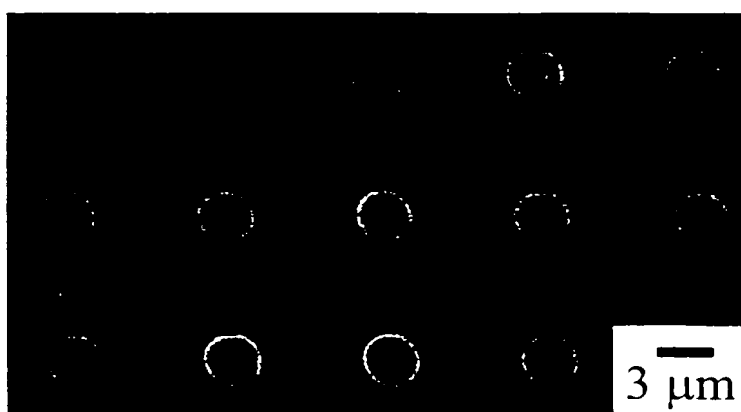


Fig. 16



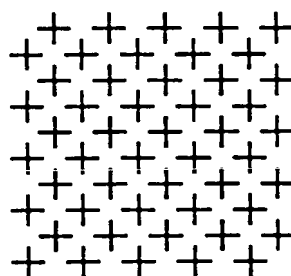


Fig. 17

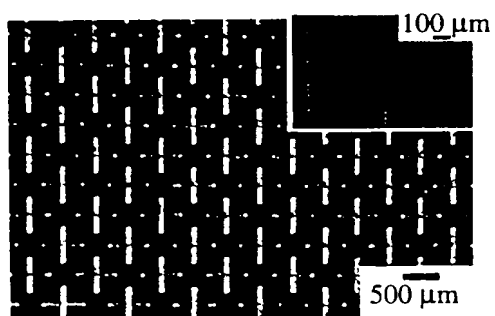
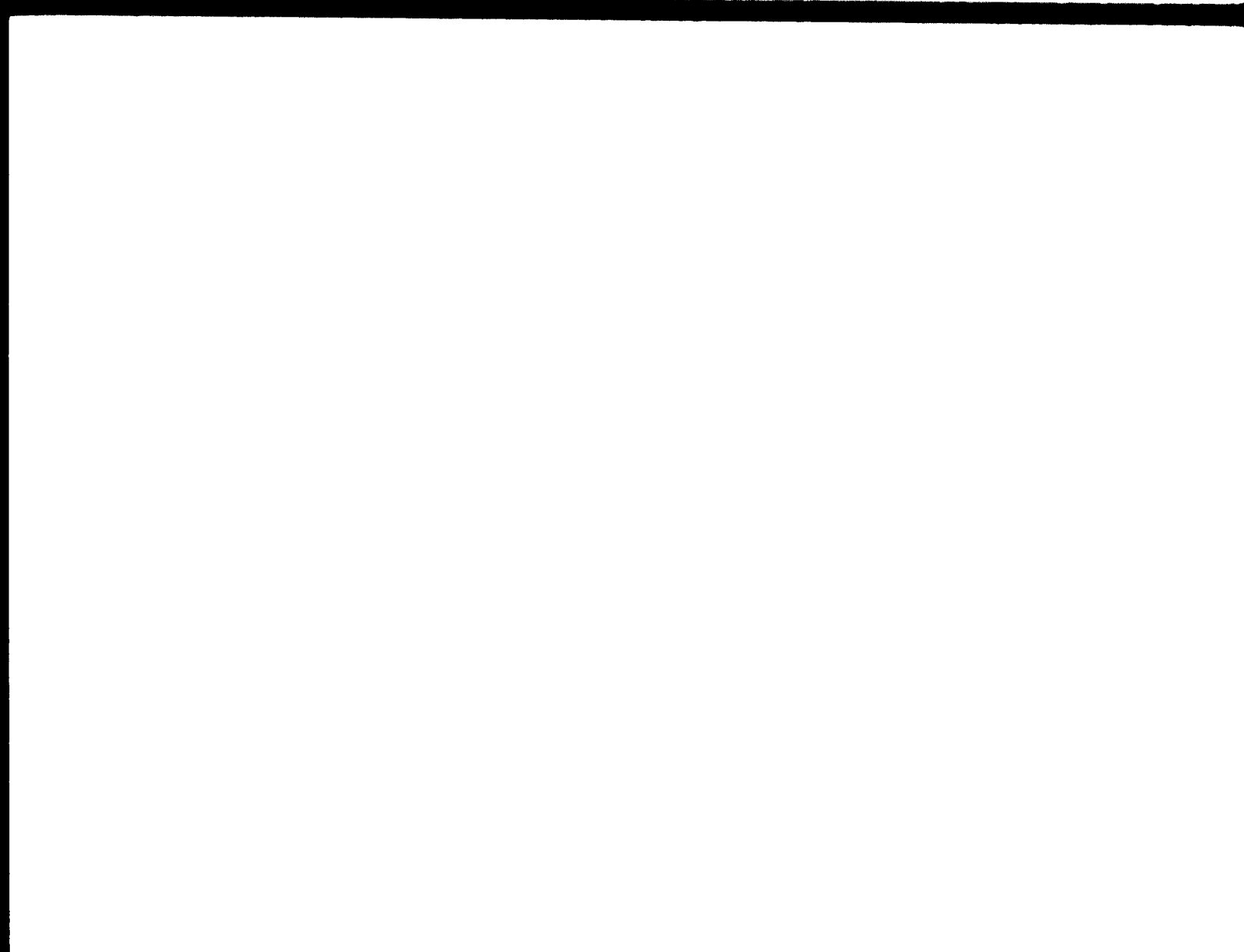
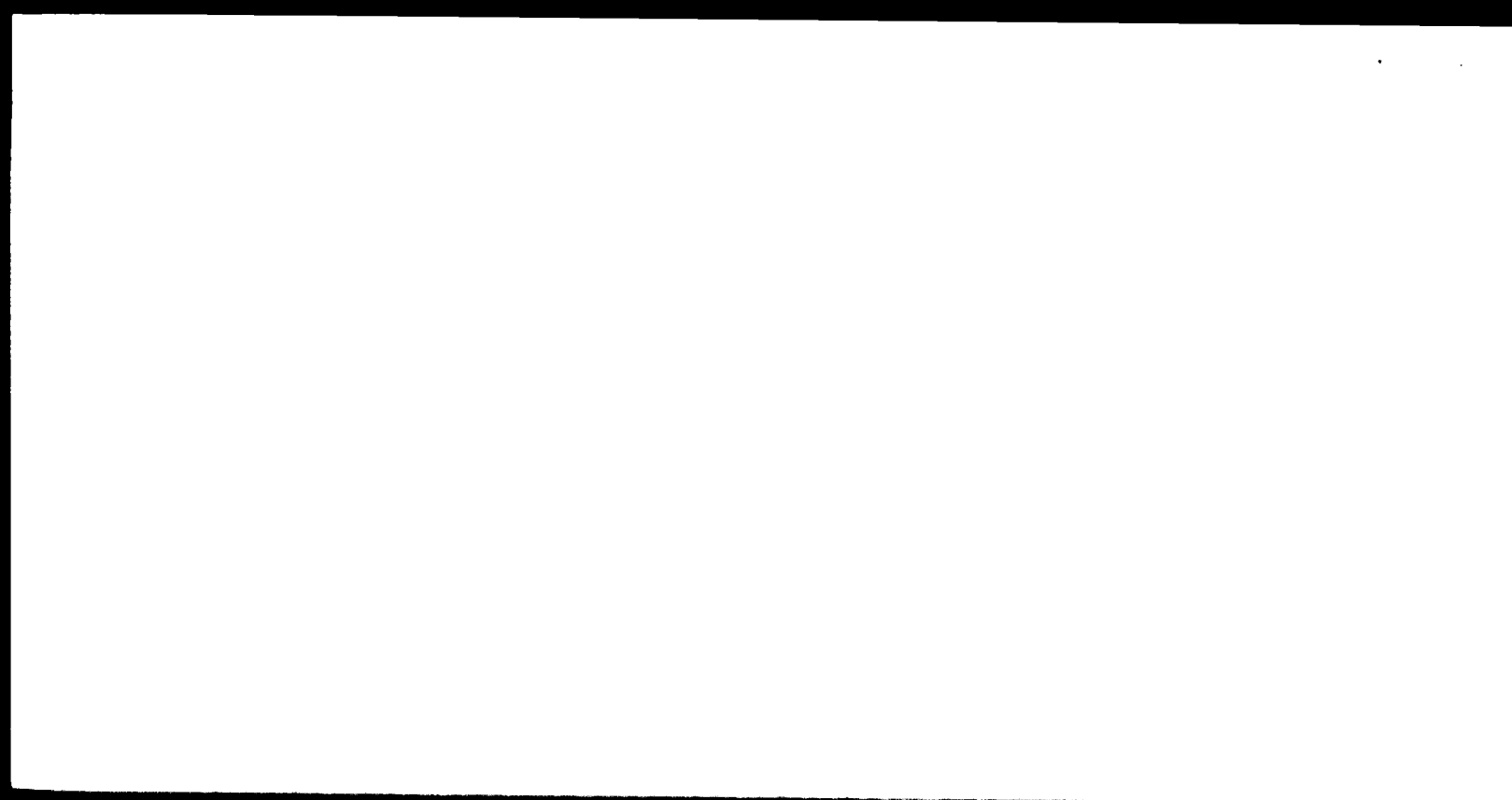


Fig. 18



# INTERNATIONAL SEARCH REPORT

National Application No  
PCT/US 99/08623

|  |  |   |
|--|--|---|
| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br>IPC 6    G03F7/00    G03F1/00    G03F7/12    B41C1/14  |  |   |
| According to International Patent Classification (IPC) or to both national classification and IPC  |  |   |
| <b>B. FIELDS SEARCHED</b><br>Minimum documentation searched (classification system followed by classification symbols)<br>IPC 6    G03F    B41C  |  |   |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  |  |   |
| Electronic data base consulted during the international search (name of data base and, where practical, search terms used)   |  |   |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>  |  |   |
| Category *   | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No.   |
| X  | DE 38 41 317 A (NOKIA<br>UNTERHALTUNGSELEKTRONIK)<br>13 June 1990 (1990-06-13)<br><br>the whole document<br>---  | 1-21,<br>23-28,<br>34-58,<br>64-66  |
| X  | US 4 093 754 A (PARSONS ROBERT C)<br>6 June 1978 (1978-06-06)<br><br>the whole document<br>---   | 1-28,42,<br>44,48,<br>49,51,52  |
| X  | ANONYMOUS: "Lift Off Technique for High<br>Temperature Metal Depositions. December<br>1972."<br>IBM TECHNICAL DISCLOSURE BULLETIN,<br>vol. 15, no. 7, page 2305 XP002113071<br>New York, US<br>the whole document<br>---<br><div style="text-align: center;">-/-</div> | 1,51,66   |
| <div style="display: flex; justify-content: space-between;"> <span><input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.</span> <span><input checked="" type="checkbox"/> Patent family members are listed in annex.</span> </div>  |  |   |
| * Special categories of cited documents:   |  |   |
| <div style="display: flex;"> <div style="flex: 1;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div> |  |   |
| Date of the actual completion of the international search<br><br><div style="text-align: center;">24 August 1999</div>   |  | Date of mailing of the international search report<br><br><div style="text-align: center;">03/09/1999</div> |
| Name and mailing address of the ISA<br>European Patent Office, P B 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx 31 651 epo nl,<br>Fax: (+31-70) 340-3016   |  | Authorized officer<br><br><div style="text-align: center;">Haenisch, U</div>                                |

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/08623

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT |  |                       |
|--|--|-----------------------|
| Category   | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
| X  | PATENT ABSTRACTS OF JAPAN<br>vol. 014, no. 544 (C-0784),<br>4 December 1990 (1990-12-04)<br>& JP 02 232238 A (TOKUYAMA SODA CO LTD),<br>14 September 1990 (1990-09-14)<br>the whole document<br>---- | 67-82                 |
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| A  | US 5 665 496 A (ANDO MASAYUKI ET AL)<br>9 September 1997 (1997-09-09)<br>-----   |                       |



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Information on patent family members

International Application No

PCT/US 99/08623

| Patent document<br>cited in search report |   | Publication<br>date | Patent family<br>member(s)                    | Publication<br>date                    |
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**CORRECTED VERSIONS OF PAMPHLETS**  
**VERSIONS CORRIGÉES DE BROCHURES**

Corrected versions of the pamphlets, identified below by their international publication number, have been published on the same date as the present issue of the PCT Gazette.

Des versions corrigées des brochures, identifiées ci-dessous par leur numéro de publication internationale, ont été publiées à la date de parution du présent numéro de la Gazette du PCT.

| International Publication Numbers<br>Numéros de publication internationale | International Application Numbers<br>Numéros des demandes internationales | Corrections   |
|--|---|---|
| WO 98/50365  | PCT/AU98/00312  | page 71, claims, added<br>page 71, revendications, ajoutée  |
| WO 98/51221  | PCT/CH98/00142  | pages 1/2-2/2, drawings, added<br>pages 1/2-2/2, dessins, ajoutées  |
| WO 98/51726  | PCT/US98/09818  | page 57, claims, added<br>page 57, revendications, ajoutée  |
| WO 98/55483  | PCT/DK98/00232  | page 89, description, added<br>page 89, description, ajoutée  |
| WO 99/46400  | PCT/US99/05538  | pages 1/13-13/13, drawings, replaced by new pages 1/13-13/13; due to late transmittal by the receiving Office<br>pages 1/13-13/13, dessins, remplacées par de nouvelles pages 1/13-13/13; en raison de la transmission tardive par l'office récepteur |
| WO 99/46606  | PCT/US99/05310  | pages 1/5-5/5, drawings, replaced by new pages 1/5-5/5; due to late transmittal by the receiving Office<br>pages 1/5-5/5, dessins, remplacées par de nouvelles pages 1/5-5/5; en raison de la transmission tardive par l'office récepteur             |
| WO 99/47946  | PCT/US99/05834  | pages 1/6-6/6, drawings, replaced by new pages 1/6-6/6; due to late transmittal by the receiving Office<br>pages 1/6-6/6, dessins, remplacées par de nouvelles pages 1/6-6/6; en raison de la transmission tardive par l'office récepteur             |
| WO 99/49793  | PCT/US99/07115  | pages 1/31-31/31, drawings, replaced by new pages 1/32-32/32; due to late transmittal by the receiving Office<br>pages 1/31-31/31, dessins, remplacées par de nouvelles pages 1/32-32/32; en raison de la transmission tardive par l'office récepteur |
| WO 99/49930  | PCT/US99/06804  | pages 1/7-7/7, drawings, replaced by new pages 1/7-7/7; due to late transmittal by the receiving Office<br>pages 1/7-7/7, dessins, remplacées par de nouvelles pages 1/7-7/7; en raison de la transmission tardive par l'office récepteur             |
| WO 99/51773  | PCT/US99/07203  | pages 1/6-6/6, drawings, replaced by new pages 1/6-6/6; due to late transmittal by the receiving Office<br>pages 1/6-6/6, dessins, remplacées par de nouvelles pages 1/6-6/6; en raison de la transmission tardive par l'office récepteur             |
| WO 99/52945  | PCT/US99/08395  | pages 1/12-12/12, drawings, replaced by new pages 1/15-15/15; due to late transmittal by the receiving Office<br>pages 1/12-12/12, dessins, remplacées par de nouvelles pages 1/15-15/15; en raison de la transmission tardive par l'office récepteur |
| WO 99/53618  | PCT/US99/07943  | pages 1/5-5/5, drawings, replaced by new pages 1/5-5/5; due to late transmittal by the receiving Office<br>pages 1/5-5/5, dessins, remplacées par de nouvelles pages 1/5-5/5; en raison de la transmission tardive par l'office récepteur             |
| WO 99/54786  | PCT/US99/08623  | pages 1/15-15/15, drawings, replaced by new pages 1/11-11/11; due to late transmittal by the receiving Office<br>pages 1/15-15/15, dessins, remplacées par de nouvelles pages 1/11-11/11; en raison de la transmission tardive par l'office récepteur |

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